$MgSiO_3$ minerals

ALLEN et al
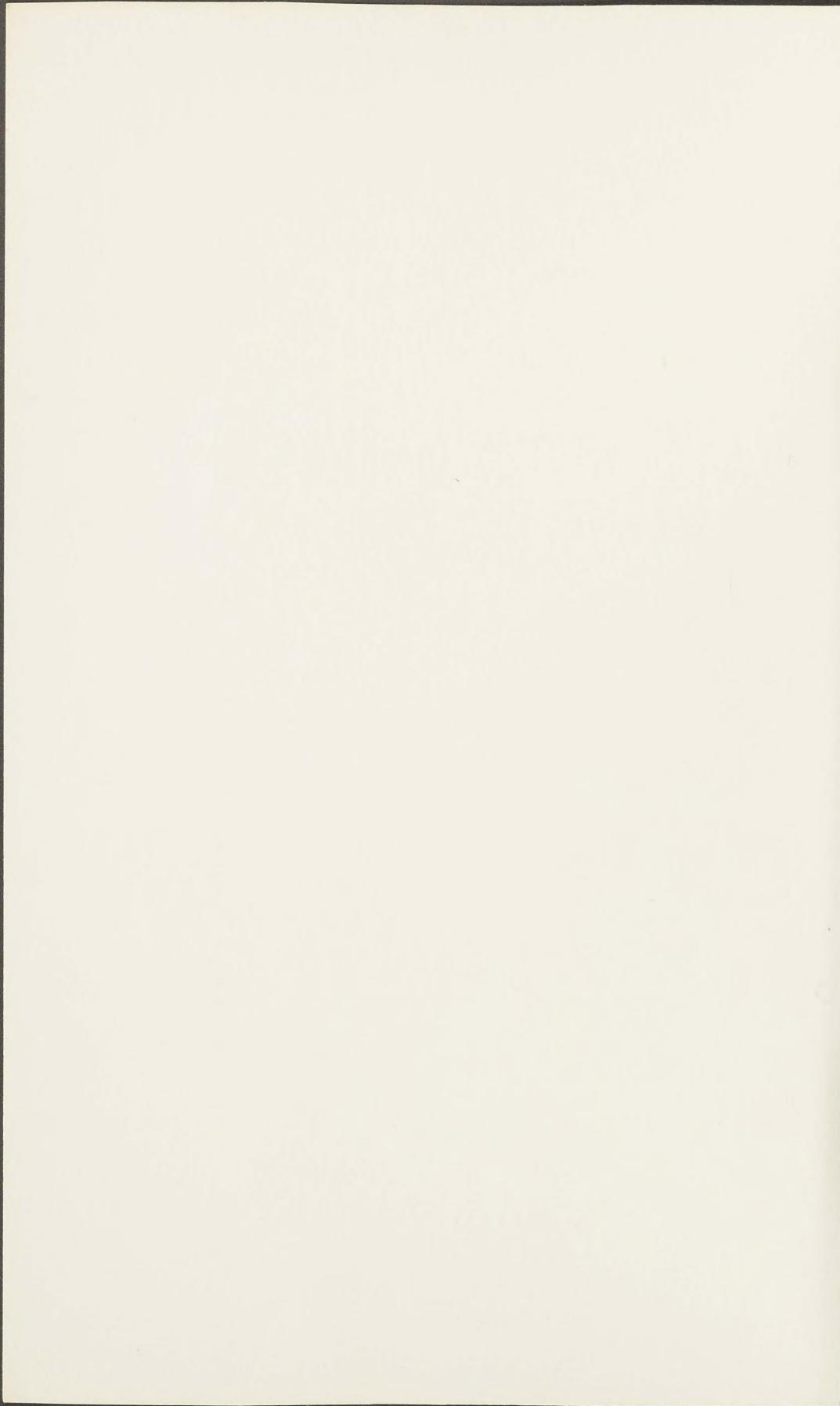
MINERALS OF THE COMPOSITION MgSiO₃;

A CASE OF TETRAMORPHISM.

By E. T. ALLEN, FRED EUGENE WRIGHT and J. K. CLEMENT.
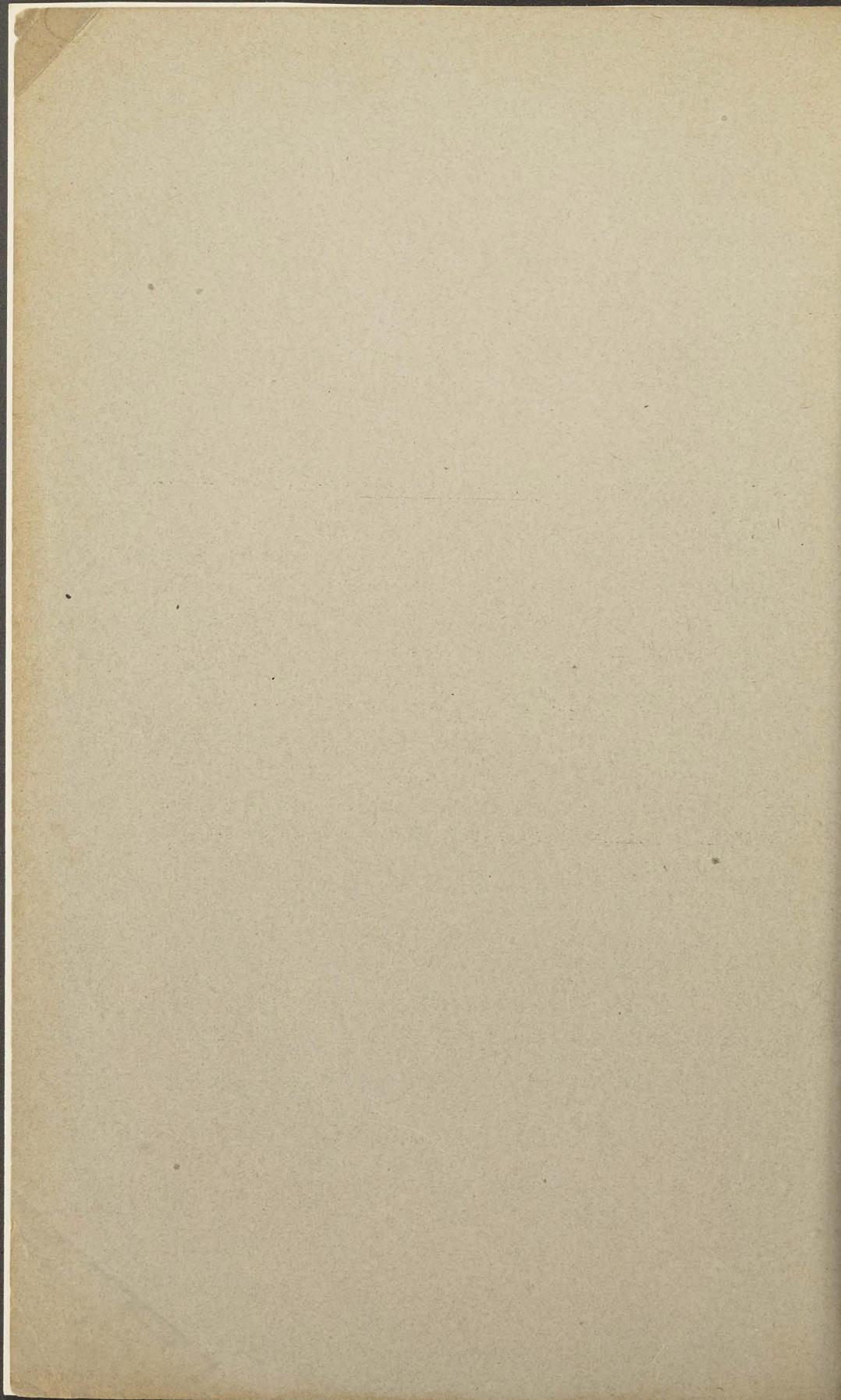
Art. XXXVII.—*Minerals of the Composition MgSiO₃; A Case of Tetramorphism ;* by E. T. Allen, Fred Eugene Wright and J. K. Clement.

Part I.—Formation and Properties of the Four Crystal Forms.

The study of magnesium silicate, to which the following pages are devoted, is part of a general investigation of the pyroxene and amphibole groups, and had for its immediate object the preparation of its several crystal forms, the determination of the conditions under which these may be produced, their relative stability, and the measurement of their accessible constants. A combination of accurate data of this kind with the geologic study of the occurrence of minerals in nature constitutes the only reliable basis for the science of mineral genesis.

The materials for this synthetic work consisted of the purest quartz and magnesia which could be obtained. The quartz contained about 0.1 per cent of non-volatile impurities and the magnesia only a few hundredths of one per cent of ferric and calcium oxides. Some slight additional contamination, however, usually resulted from repeated fusion of the same material. In one of the preparations, which had been remelted many times, we found by direct analysis 0.3 per cent of ferric and aluminic oxides and practically no other impurities.

	Found.	Calculated for $MgSiO_3$.
SiO_2	59.85%	60.00%
MgO	39.77	40.00
Al_2O_3 and Fe_2O_3	$.30$	
	99.92	100.00

Four distinct crystal forms of magnesium metasilicate were found to exist and to be reproducible at will in the laboratory. These forms agree in their optical and other physical properties closely with the following minerals: (1) the monoclinic magnesian pyroxene*; (2) enstatite ; (3) kupfferite† ; (4) a monoclinic amphibole corresponding to kupfferite; our products form in fact the end members of certain solution series toward which the natural minerals approach, and sometimes almost

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* Discovered by Fouqué and Lévy in certain meteorites (Bull. Soc. Min., p. 279, 1881) and by the authors in the Bishopville meteorite. We shall show later that this form differs considerably in its axial ratio $c : a$ from other pyroxenes.

† See Hintze, Mineralogie, Bd. II, p. 1196.

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reach, when practically free from impurities. The conditions of formation and the properties of these four minerals will first be described; their relations to one another will then be considered in a subsequent portion of the paper.

1. *Monoclinic Pyroxene.*—This form of magnesium silicate is the product usually obtained from fusion, though small but variable quantities of enstatite and kupfferite commonly crystallize with it. Ebelmen,[*] who was the first to synthesize the monoclinic magnesium silicate, accomplished it by melting magnesia and silica with boric anhydride. The latter substance served as a flux and was evaporated later by long-continued heating at a high temperature. Hautefeuille[†] reached the same result by dissolving amorphous silica in molten magnesium chloride with partial exclusion of moisture; Stanislas Meunier[‡] effected its synthesis through the action of silicon chloride and water vapor on metallic magnesium. Hautefeuille, Daubrée and other earlier observers mistook this form for enstatite. Their work was done at a time before modern microscopic methods had been developed, and their conclusions were therefore based chiefly on chemical and morphological evidence, which misled them, as was proved later by Fouqué and Lévy[§] and by Vogt,[||] who examined the original preparations of Ebelmen and Hautefeuille preserved in the museum of the Collège de France.

In our own experiments we have observed the formation of the monoclinic pyroxene in several different ways: (1) from a melt of the same composition; (2) by heating the glass to a temperature above 1300°; (3) by heating any of the other crystalline forms; (4) from the action of molten magnesium chloride or tellurite on amorphous silica; (5) by recrystallizing magnesium silicate from a flux of magnesium chloride, magnesium vanadate, calcium vanadate, or tellurium dioxide.

(1.) The first method, except under conditions of slow cooling, yields crystalline aggregates, usually in radial spherulites, consisting chiefly of the monoclinic form, generally intermixed with more or less enstatite and kupfferite; but if the molten silicate crystallizes at a temperature only slightly below the melting point, an operation which can readily be carried out in the electric resistance furnace, the product is homogeneous, and consists entirely of the monoclinic form. This is the best method for preparing this substance in quantity, though the crystals are not individually well developed.

(2.) The product obtained by heating the glass to 1300° or

* Ann. Chim. Phys. (3), xxxiii, 58, 1851.   † Ibid. (4), iv, 174, 1865.
‡ Comptes Rendus, xc, 349, 1880.
§ Synthèse des Minéraux et des Roches, p. 107.
|| Mineralbildung in Schmelzmassen, p. 71. These observers also studied preparations of their own, and Vogt has described the occurrence of the same mineral in blast furnace slags.

more was similar to that from the melt, with the difference that the spherulites and their component fibers were smaller.

(3.) All other forms of magnesium silicate change to the monoclinic pyroxene by heating to temperatures from 1150° upwards, the temperature depending on the original form and the time allowed.

(4.) A repetition of Hautefeuille's work proved the correctness of his observations except as to the crystal form of his product. Magnesium chloride dissolves amorphous silica in the presence of small quantities of moisture

$$(MgCl_2 + H_2O + SiO_2 = MgSiO_3 + 2HCl)$$
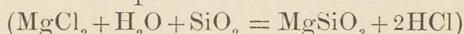
but exerts little action on quartz. Instead of the chloride one may use the tellurite, an easily fusible salt which acts as readily on the silica as the chloride, has the advantage of being less susceptible to the action of water, and the disadvantage of being readily reducible to the metal and attacking the platinum crucible in which the fusion is made. The following equation represents the reaction:

$$MgTeO_3 + SiO_2 = MgSiO_3 + TeO_2.$$
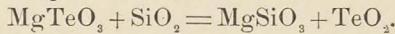
The tellurous oxide is volatilized at the temperature of the experiment (700°–800°). The crystals obtained by both magnesium chloride and magnesium tellurite were generally small and not so well developed as those crystallized by method (5).

(5.) A considerable number of fluxes were found to dissolve magnesium silicate at temperatures of 800°–1000° and to precipitate it again in crystals of the monoclinic variety, a fact which has an important bearing on the question of the relative stability of the different crystal forms. It soon became evident, moreover, that certain fundamental questions connected with the pyroxene series could only be settled by the crystallographic study of the monoclinic form, so that we made a rather extensive investigation of the conditions necessary to obtain from these fluxes crystals sufficiently well developed for measurement. Among these solvents which did not prove satisfactory, we may mention calcium chloride, sodium sulphate, sodium chloride and potassium chloride. The last two gave small yields of an unpromising crystalline product which was not fully investigated. The fusible silicates of lead, sodium and potassium* all gave glasses. In point of time, we first tried fusible magnesium salts as probably best suited to dissolve the silicate without decomposing it. Of these there are the tellurite, the vanadate and the chloride.

With Magnesium Tellurite.—As stated above, the tellurite is a readily fusible salt, and though not soluble in water, it

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* It was found later that a solution of magnesium silicate in a small quantity of sodium and potassium silicates yields good crystals of enstatite.

may be decomposed with hydrochloric acid, so that we expected to be able to remove the excess of reagent from the silicate without difficulty. The silicate and tellurite were therefore mixed in about equal quantities (about 5 grams of each) and heated in a covered platinum crucible by means of a resistance furnace to prevent reduction of the tellurite. At 1000°–1100° some monoclinic pyroxene was obtained, but the greater part of the product proved to be fosterite, formed by the decomposition of the tellurite and the volatilization of tellurous acid, which partly condensed on the cooler parts of the furnace. The equations:

$$MgTeO_3 + SiO_2 = TeO_2 + MgSiO_3.$$
$$2MgTeO_3 + SiO_2 = 2TeO_2 + Mg_2SiO_4.$$
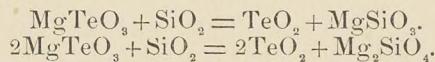
represent these reactions. The crystals obtained by this method are not well formed and it is difficult to remove the tellurium completely.

The above reaction led us to believe that magnesium silicate might perhaps crystallize from molten tellurous oxide, but, though well developed monoclinic prismatic crystals were occasionally obtained, most of the silicate was apparently decomposed by this method.

With Magnesium Vanadate.—In some earlier experiments on wollastonite carried out in this laboratory,[*] it was found that calcium silicate could be readily dissolved and recrystallized from molten calcium vanadate, the excess of which could be easily removed by alternate treatment with very dilute hydrochloric acid and ammonia; we therefore expected to be more successful with magnesium vanadate than with tellurite. The conditions followed in the beginning were similar to those which had worked so well with calcium silicate, but as the first results were not satisfactory, we eventually tried various proportions of silicate and vanadate at temperatures ranging from 800° to 1050°. At the lower temperature monoclinic crystals of rather poor development were obtained, but at the higher temperature a good deal of fosterite always accompanied it, and vanadic anhydride was evidently set free, as the product was colored a dark brown. Most of ·the vanadate and vanadic acid can be removed by cold dilute hydrochloric acid and hot concentrated ammonia, but several per cent are generally retained by the silicate.

With Calcium Vanadate.—In spite of our apprehension of double decomposition with salts containing no common ion, we found that calcium vanadate dissolved and crystallized magnesium silicate unchanged in composition and sufficiently

* Allen, White and Wright, this Journal (4), xxi, 97, 1906.

well developed for goniometric measurement. The best results were obtained by following the conditions just referred to for the formation of wollastonite.*
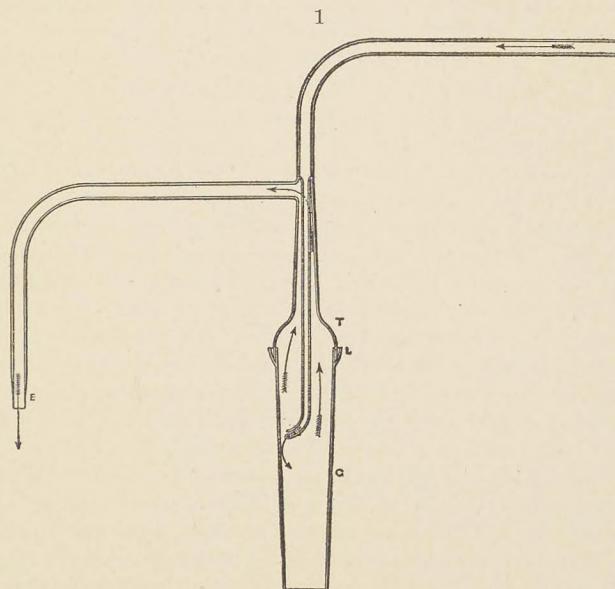
With Magnesium Chloride in a stream of Hydrochloric Acid Gas.—These experiments were carried out in the platinum crucible fig. 1, invented by Professor Gooch for the determination of water in difficultly decomposable silicates.†
It consists essentially of a long crucible slightly conical in form, with a collar around the top so constructed as to leave a narrow groove between it and the cap which covers the crucible. Into this groove sodium tungstate can be melted to form an air-tight seal. The cap is so constructed as to permit the passage of a current of gas through the crucible.

Two or three grams of magnesium silicate were first put into the dry uncovered crucible. A quantity of anhydrous magnesium chloride, prepared by the decomposition of magnesium-ammonium chloride‡, was heated just before the experiment in a current of dry hydrochloric acid gas, cooled and dropped immediately into the crucible. The cover was then

* Loc. cit.
† Bull. U. S. Geol. Survey, No. 176, p. 42.
‡ It is not easy to prepare magnesium chloride in quantity free from oxide ; the product of the decomposition of magnesium-ammonium chloride, as this is ordinarily carried out, requires a thorough treatment with dry hydrochloric acid gas.

sealed on without delay and the crucible connected with a generator furnishing a slow stream of well-dried hydrochloric acid gas.* In our experiments the crucible was heated over a burner to about 1000°. It was not possible to measure the temperature inside the crucible during the progress of the work, but in the empty crucible a bare thermoelement, touching the bottom, read 1050° just before the charge was inserted. This was therefore the approximate temperature in the hottest part of the crucible. In the first experiment the outlet was left unprotected against moisture. After four days the silicate was found to be converted entirely into fosterite.

In all the later experiments with magnesium chloride, the outlet tube of the crucible was well guarded by a U-tube containing sulphuric acid and a straight tube containing calcium chloride to prevent the passage of moisture into the crucible. At temperatures between 1000°–1100° (in the hottest part of the crucible) we invariably obtained some fosterite and periclase as by-products, but in the main the substance crystallized as the monoclinic pyroxene. This method gives by far the best results of any we have discovered.

Optical Constants of Fosterite.—Inasmuch as crystals which appeared to be fosterite were often obtained in the course of our work,—crystals which by optical tests alone it was found difficult to distinguish from minute crystals of enstatite, it seemed advisable to determine the crystallographic constants of these from magnesium chloride. The crystals were colorless, transparent, and about $0.2 \times 0.1 \times 0.1^{mm}$ in size, short prismatic in habit, doubly terminated, and similar to natural fosterite in appearance. The cleavage, perfect after 001 and 010, was obtained by actual fracture of a crystal under the

TABLE I.

No.	Letter.	Symbol.	Miller.	Measured.		Goldschmidt.[†]	
				ϕ	ρ	ϕ	ρ
1	b	0	001	- - - -	$0°\ 00'$	- - - -	$0°\ 00'$
2	a	0∞	010	$0°\ 00'$	90 00	$0°\ 00'$	90 00
3	n	∞	110	64 26	90 00	65 01	90 00
4	d	10	101	90 00	51 37	90 00	51 32
5	k	02	021	0 00	49 44	0 00	49 39
6	e	11	111	65 51	54 19	65 01	54 15

* The platinum is often slightly attacked during the fusion. Whether this comes from the decomposition of the chloride by oxygen :

$$MgCl_2 + O + MgSiO_3 = Mg_2SiO_4 + 2Cl \ (?)$$
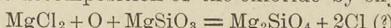
has not been worked out. When the magnesium coloride is mixed with sodium chloride, the platinum is very strongly attacked.

† V. Goldschmidt, Winkeltabellen, Berlin, p. 251–252, 1897.

microscope. The crystal faces were well defined, giving fair
reflection signals on the goniometer. The measurements were
made on a two-circle goniometer with reducing attachment,
and the results were found to agree fairly well with the same
constants for natural fosterite. The crystals measured were
too small to permit a very accurate measurement of the angles
(Table I).

The crystal represented in fig. 2
measured $\cdot15^{mm}$ in length and $0\cdot12^{mm}$
in thickness, was transparent, colorless,
and well developed on all sides. The
development was noticeably unsym-
metrical and the quality of the dif-
ferent faces varied considerably. The
indices of refraction were determined
by Schroeder van der Kolk's method
of refractive liquids in which the pos-
sible error does not exceed $\pm\cdot003$; $a =$
$1\cdot645 \pm \cdot003$, $\beta = 1\cdot656 \pm \cdot003$, $\gamma =$
$1\cdot668 \pm \cdot003$. Birefringence $= 0\cdot023$
$\pm \cdot006$. The interference colors are
bright, usually of the first and second

Olivine crystal from melt
of MgSiO₃ in MgCl₂.

orders. The crystals extinguish parallel to the cleavage direc-
tions. The plane of the optic axes is perpendicular to the most
perfect cleavage lines after 010 and to the prismatic develop-
ment of the crystal and lies in the plane 001. The optic axial
angle is very large with c the acute bisectrix. The crystals
were decomposed by hydrochloric acid with the separation of
gelatinous silica. In one preparation fosterite crystals were
observed enclosing original fragments of the pyroxene which
had not been fully dissolved by the solvent.

In a number of experiments with magnesium chloride we also
observed the formation of periclase (MgO) in well-formed
octahedra (1^{mm} in length), isotropic and of characteristic cleav-
age and refractive index $1\cdot73$.

Properties of the Monoclinic Pyroxene.—Though crystals
of monoclinic pyroxene were obtained from many fluxes and
under different conditions, as a general rule they were ex-
tremely small and could be used only in a few favorable
instances for crystallographic measurement. Crystalline aggre-
gates of this form were also readily obtained direct from
the molten silicate and then usually as large radiating spheru-
lites, the individual fibers of which were frequently 1 to 2^{cm}
long. The crystals were measured on the two-circled goniome-
ter with reducing attachment, were colorless, transparent, of
glassy luster and varied in length from $\cdot1$ to 1^{mm}, and in width
from $\cdot05$ to $\cdot5^{mm}$. An extremely small crystal of this substance

0·1^{mm} long and 0·04^{mm} wide, from a solution in calcium vanadate, was first measured.   A single fine twinning lamella after the orthopinacoid was observed under the microscope, but could not be detected on the goniometer. The reflection signals were very faint and the recorded angles fluctuated somewhat in consequence.   The largest and best developed crystals (fig. 3) were produced by heating magnesium metasilicate with magnesium chloride in a stream of dry hydrochloric acid gas.   Six different crystals obtained by this method were measured and the forms: c (001) (?), a (100), b (010), m (110), n (120), l (250) (?), k (310), r (210) (?), o (111), i (121), p ($\bar{1}$01), s ($\bar{1}$11), e ($\bar{1}$21), (103) (?), and ($\bar{1}$03) (?) observed. Several of these forms, c (001) (?), r (210) (?), l (250) (?), (103), ($\bar{1}$03), were noted only once, gave poor reflection signals, and are therefore uncertain. The faces in the prism zone were much better developed than the terminal forms and, although small, usually gave sharp reflection signals and concordant angles.   The prismatic cleavage angle (110 : $\bar{1}$10 = 88° 08′) thus obtained has a probable error of only ± 3′. The terminal faces, on the other hand, were much smaller, less clearly defined and seriously interrupted by intergrown twinning lamellae, so that the axial ratio obtained for the vertical axis is of a lower order of certitude.

In order to show graphically the variations in the angles observed in the different crystals, a gnomonic projection of the results from the six crystals measured is presented in figure 4. The irregularity in the position of many of the projection points is due in large measure to the indistinct reflection signals obtained.   Transitional faces were observed in several zones and have been indicated in the figure by the shaded portions of the zone lines.   They furnish an excellent criterion for the primary zones and nodes which dominate the development of the forms bounding the crystal.

On comparing these crystallographic measurements with the angles given for enstatite and diopside, it was found that the prism angles, and therefore the axial ratio $a : b$ for the three minerals, were very similar, while the angles for the terminal faces differ so noticeably that they cannot be ascribed to experimental error alone.   The axial ratio $a : b : c$ for

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Mg-pyroxene.
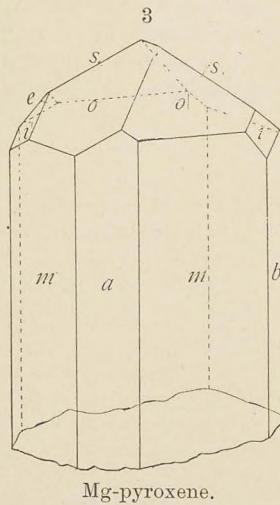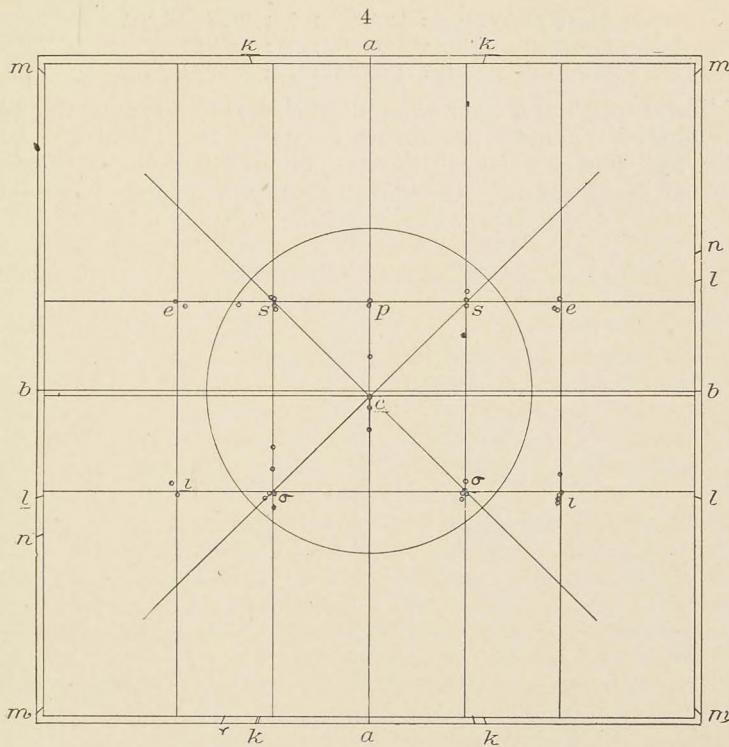
TABLE II.*

No.	Letter.	Symbol.	Miller.	φ		ρ	
1	c (?)	0	001	———		2° 00′	
2	a	∞ 0	100	90	00	90	00
3	b	0 ∞	010	0	00	"	
4	m	∞	110	44	04	"	
5	n	∞ 2	120	23	07	"	
6	l (?)	∞ $\frac{5}{2}$	250	17	56	"	
7	k (?)	3 ∞	310	70	44	"	
8	r	2 ∞	210	66	54	"	
9	o	1	111	43	29	39	58
10	i	12	121	24	58	52	11
11	p	$\bar{1}$0	$\bar{1}$01	$\bar{9}$0	00	29	09
12	s	$\bar{1}$1	$\bar{1}$11	$\bar{4}$6	52	40	21
13	e	$\bar{1}$2	$\bar{1}$21	$\bar{2}$8	30	53	10
14	(?)	$\frac{1}{3}$0	103	90	00	11	55
15	(?)	$\frac{1}{3}$0	$\bar{1}$03	90	00	12	55

* The angles given in this table are the weighted averages of the angles measured.

$$\text{Mg-Pyroxene} = 1\cdot033 \; : \; 1 \; : \; 0\cdot77 \quad \pm \cdot01$$
$$\text{Enstatite} \quad = 1\cdot0308 \; : \; 1 \; : \; 0\cdot5885$$
$$\text{Diopside} \quad = 1\cdot0934 \; : \; 1 \; : \; 0\cdot5894$$

These relations appear even more clearly in a gnomonic projection of the most prominent forms of the three minerals (fig. 5). The character of the projection of the principal forms of the Mg-pyroxene, although distinctly monoclinic in aspect,
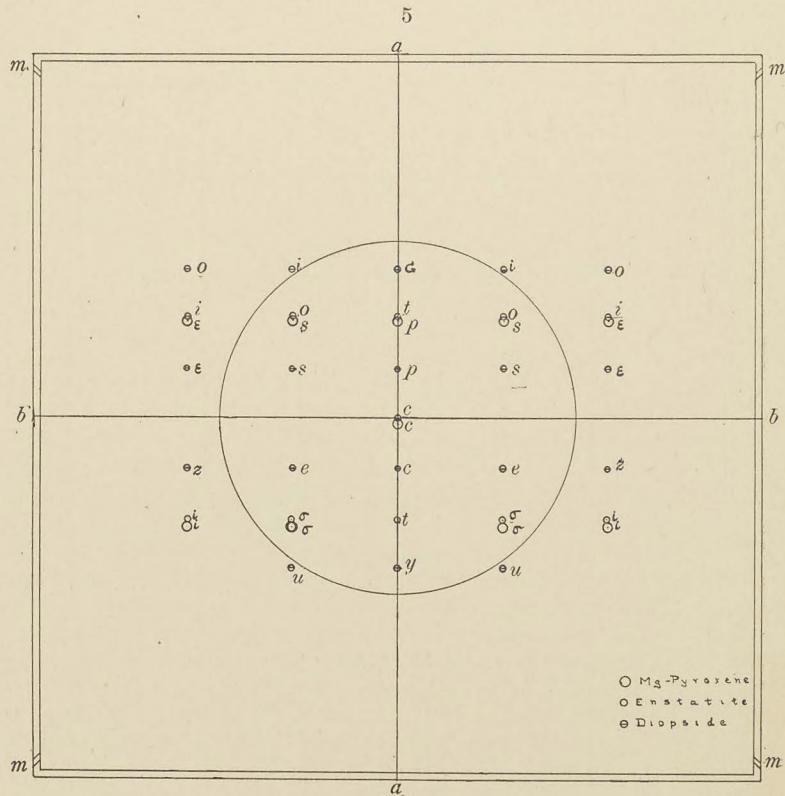
is closely related to that of the enstatite projection, and only vaguely to that of diopside. It is clear from the figure that the principal zones for diopside do not coincide with those of the Mg-pyroxene, but are located in an intermediate position. Though the symbols of the latter might be expressed very roughly in terms of diopside by choosing for the basal pinacoid of the Mg-pyroxene the possible form (102) in place of the present basal plane, thus complicating the entire set of symbols, the differences in distances between corresponding forms are even then too great to justify this change, and cast, there-

fore, grave doubt on a possible isomorphic relation between the two substances, especially when the different zonal development of the two is also taken into consideration. The investigation of this important question is still in progress.

Polysynthetic twinning after the orthopinacoid occurs almost invariably and is apparently as characteristic of this particular pyroxene as twinning according to the albite law is characteristic of the plagioclase feldspars : between crossed nicols the sections frequently bear a striking resemblance to those of plagioclase.

A peculiar type of these monoclinic crystals was observed in several of the preparations ; they were developed in flat tabular form after the orthopinacoid, and in consequence of this lay invariably on this face when immersed in one of the refractive liquids. Thus the extinction was of course always parallel and might have led to erroneous conclusions in regard to the crystal system and confusion with enstatite, if special pains had not been taken to test their behavior in other positions. The crystals were accordingly imbedded in thickened Canada balsam, in which medium they could be slowly turned by moving the cover glass. The thin upturned edges then showed the polysynthetic twinning after 100, and the extinction angles characteristic of this form. In the examination of later preparations, a device for turning the crystals in any direction and in liquids of equal refractive index was constructed and proved satisfactory. The immersion method in Canada balsam, however, is less complex and usually answers equally well.

The hardness of the monoclinic pyroxene is about 6 ; the crystals are only slightly attacked by acids.

The refractive indices were determined by the immersion method of Schroeder van der Kolk :

$$a = 1\cdot647 \pm \cdot003, \ \beta = 1\cdot652 \pm \cdot003, \ \gamma = 1\cdot658 \pm \cdot003 \ ;$$

the birefringence is not strong—about ·01. The extinction angle on the clinopinacoid—remarkably low for a pyroxene—was carefully measured on well-developed crystals obtained from a fusion of the metasilicate in magnesium chloride. These crystals were twinned polysynthetically and the extinction angle was obtained, as in the feldspars, by using the symmetrical extinction angles of adjacent lamellae. An average of 25 readings gave $c : c = 21°\cdot8$ (with extreme values of $19°\cdot5$ and $24°\cdot5$). Measurements in sodium light were also made with practically the same result. The dispersion of the bisectrices was found to be very slight. The plane of the optic axes lies in the clinopinacoid ; the optical axial angle is very large. The optical character is positive and was ascer-

tained by observing in convergent polarized light on a section after 010 the direction in which the dark hyperbolae of the interference figure emerge from the field on revolving the stage, this direction being that of the acute bisectrix.* The result was, furthermore, confirmed on a section normal to an optic axis. An attempt was made to measure the optic axial angle on such a section by the graphic method recently described by F. Becke,† but the fine intercalated twinning lamellae affected the sharpness of the figure to such an extent that valid numerical results were out of the question. The black axial bar of the figure, however, is only slightly curved in the diagonal position and indicates a large axial angle.

The disturbing influence of the twinning lamellae was furthermore felt in some unsuccessful attempts to etch the prism faces with hydrochloric acid. The fine lamellae apparently destroyed the continuity of any larger etch figures which might otherwise have formed.

The specific gravity at 25° was determined on preparations from the melt by the method of Day and Allen :‡

Specific gravity of the Monoclinic Pyroxene, H_2O at 25° = 1.

Preparation I.	Preparation II.
3·191	3·194
3·192	3·191
Average,	3·192

Melting Point of Magnesium Metasilicate.—The melting point was determined by the Frankenheim method, using a control element, as described by Allen, White and Wright.§

The results are contained in Table III.

TABLE III.

Element E.	Element K.	
1521·3°	1521·3°	Both elements in same porcelain tube
1519·7	1522·2	Both elements in same porcelain tube
	1521·	
Mean,	1521°.	

After every experiment, elements E and K were compared with the standard element, H, which was protected from contamination and deterioration due to absorption of iridium vapor, by a tube of pure platinum. The heating coils of the furnace, which we have used heretofore, have been wound with platinum wire containing 10 per cent of iridium. It has been found that at temperatures of 1200° or more, the iridium

* Wright, F. E., this Journal (4), xvii, p. 385, 1904.
† Becke, F., Tscherm. Min. petr. Mitth., xxiv, 32–49, 1905.
‡ This Journal (4), xix, 93, 1905.   § Loc. cit.

volatilizes and is absorbed by the thermoelements.* This contamination produces a drop in the electromotive force of the element which with continuous usage may result in a large aggregate error. An unglazed porcelain tube is quite permeable to the vapor. For exact measurements above 1000°, therefore, the thermoelement must be protected by an enclosing tube of pure platinum in the hot portion of the furnace, whenever a furnace coil containing iridium is used.

The maximum difference of any two determinations is 2·5°. The absolute value of the melting temperature is based on extrapolation from the copper melting point.

II. *Orthorhombic Pyroxene. Enstatite.*—So far as our knowledge goes, pure enstatite, free from other polymorphic forms, has never been prepared. Ebelmen and Hautefeuille obtained some true enstatite which was afterwards proved to be mixed with the monoclinic variety. The crystals of Meunier,† who believed that he had synthetized enstatite, were shown by Fouqué and Lévy to be monoclinic. Daubrée's product,‡ which was obtained by melting portions of meteorites, was, according to his own statement, too opaque for optical examination, so that he could not say whether his crystals were orthorhombic or monoclinic.

The same experimenter also melted olivine with 15 per cent silica, and obtained a crystalline cake, the interior of which consisted of a fibrous mass which was unattacked by acids, and "which had the properties of enstatite."§ Not only is no proof of the orthorhombic nature of these fibers offered, but we know from our own experiments that Daubrée's conditions must have yielded a product which consisted in the main of the monoclinic form. Fouqué and Lévy, in the effort to reproduce meteorites by artificial means, succeeded in crystallizing enstatite intermixed with a small amount of monoclinic pyroxene in the following way: 12 grams silica, 3 grams magnesia, and 5 to 5·5 grams ferric oxide, were melted and rapidly cooled. The cake showed arborescent crystals which by prolonged reheating at a temperature a little above the melting point of copper, developed into larger needles showing parallel extinction.

As previously stated, we also obtained enstatite in small but variable quantities from melts of magnesium silicate, except when it was slowly cooled. The crystals of enstatite thus formed were intercalated between the fibers of monoclinic pyroxene and could only be distinguished from the latter

* W. P. White, "The Constancy of Platinum Thermoelements and Other Thermoelement Problems," Phys. Rev., vol. xxii, p. 372, 1906.
† Synthèse des Minéraux et des Roches, pp. 109, 111.
‡ Compt. Rendus, lxii, 202, 1866.   § Ibid., lxii, 374, 1866.

by the aid of the microscope. The two forms resemble each other so closely in habit and optical properties that one must rely chiefly on the extinction angle to distinguish between them. In the prism zone enstatite shows parallel extinction on all planes, while the monoclinic variety extinguishes parallel only on the orthopinacoid. Inasmuch as crystals of the latter frequently show pronounced development after the orthopinacoid, their monoclinic nature can only be recognized by immersing the crystals in a viscous liquid such as Canada balsam and rolling them, log-like, and observing the extinction in the different positions.

We have succeeded in preparing enstatite which contains only slight traces of impurities by a method similar to that used in this laboratory for the preparation of pure wollastonite,* and which, as may be noted, bears considerable resemblance to the method of Fouqué and Lévy. It consists simply in crystallizing a glass of the same composition by heating it to a temperature below 1100°. The practical details of preparing this glass, however, involve considerable difficulty owing to the readiness and rapidity with which crystallization proceeds in this silicate. Not more than 10 grams of it should be used for a single charge, the temperature of the platinum containing vessel should be raised well above the melting point of the silicate, and the fusion should be instantly chilled by plunging it into cold water. Care should also be taken that the temperature is sufficiently high to melt the silicate (m. p. 1521°) and yet not high enough to melt the platinum crucible (1720°). In our earlier experiments, crucibles were ruined so frequently by partial melting that we were compelled to make some rough temperature measurements by inserting a thermoelement under the hood of the Fletcher furnace. Though the temperatures thus observed were not those of the crucible, they indicated the latter approximately, and when the readings ranged from 1500° to 1550°, the results were fairly satisfactory.

Even under these conditions, the most favorable we have found, the glass is rarely obtained entirely free from crystalline material. After the glass had been mechanically separated from the latter, small samples were crystallized at various known temperatures and the products examined microscopically.

To insure the crystallization of a glass as nearly as possible at a given temperature, the following method was used. An empty platinum crucible was placed in an electric resistance furnace, through the cover of which passed a thermoelement, reaching nearly to the bottom of the crucible, together with

* This Journal (4), xxi, 89, 1906.

an unglazed porcelain tube of about 1^{cm} inside diameter, the lower end of which was directly over the uncovered platinum crucible. The upper end of this tube was covered by a porcelain lid. (An arrangement similar to fig. 10.) The temperature of the furnace having been raised to the desired temperature, the glass, in small fragments, is then dropped through the porcelain tube into the crucible. Only small fragments can be used, for the initial temperature of the crucible is materially lowered by the introduction of any considerable mass of the cold substance, after which the heat of crystallization of a large mass of the glass will raise the temperature of the portion last to crystallize above that of the furnace. At 1150°–1200°, when small particles, each of a few milligrams weight, were used, no perceptible change in the temperature of the crucible was noted. Under such conditions about 20 seconds elapsed, and we estimated that the temperature of the crucible was reached, before crystallization began. The temperature of the glass particles, however, does no doubt rise above the temperature of the crucible, for they become more luminous during the process. It is interesting to watch the crystallization; it begins at the surface and proceeds inward with rise in temperature, which is especially noticeable when the particles are large; the outer portion contracts and squeezes out the still liquid interior in the form of hollow, rounded projections, which crystallize last, and at a higher temperature, for they are always of coarser grain. These grains bear a strong resemblance to a kernel of ordinary popped corn.

Table IV contains the results of the experiments on the crystallization of magnesium silicate glass at different temperatures by the process above described.

TABLE IV.

Crystallization of Magnesium Silicate Glass.

750°	No crystallization in 45 minutes.
900	Too fine-grained for identification.
990	" " " " "
1075	Nearly all enstatite ; presence of monoclinic form doubtful.
1125	Enstatite, with some monoclinic form.
1175	Enstatite and monoclinic form.
1225	" " " "
1275	" " " "
1300	Monoclinic form and probably some enstatite.
1325	" " " " " "

It is plain from these figures that below 1100° the product is enstatite; while not far above that point the monoclinic form begins to appear. To prepare a nearly homogeneous aggre-

gate of enstatite crystals in quantity, therefore, it suffices to crystallize the glass somewhat below 1100°, but not below 1000°, if the preparation requires microscopic identification, for the product then formed is cryptocrystalline. The enstatite was distinguished from the monoclinic form solely by its parallel extinction in the prism zone, the refractive indices of the two forms not differing sufficiently to permit the use of that method. By cooling mixtures of magnesium silicate with 10 per cent of its weight of albite, or the same amount of sodium and potassium silicates, enstatite may be obtained in long, well-developed prisms, the index of refraction of which indicates only a small quantity of dissolved albite or other foreign matter. Some experiments in this direction are described in detail farther on p. 433.

Properties of Chemically Pure Enstatite.—Thus far, we have obtained pure enstatite only in fibrous aggregates and radial spherulites which do not admit of a precise determination of its morphologic constants. It is a remarkable fact that the direction of elongation of the fibers in the small radial spherulites is not the prism axis, but another, such that the greater ellipsoidal axis a is parallel to it instead of c.

Cleavage after 110 is well marked; its angle approximates 90° and was observed under the microscope by tilting on end the individual fibers embedded in thick Canada balsam. The extinction is parallel in the prism zone and the least ellipsoidal axis c coincides with the prism axis.

The optical properties are similar to those of the monoclinic magnesium pyroxene, differing chiefly in the parallel instead of inclined extinction, lower average refractive index and smaller optic axial angle. The refractive indices were determined by the immersion method in liquids:

$$a = 1·640 \pm ·004, \beta = 1·646 \pm ·004, \gamma = 1·652 \pm .004;$$

birefringence not strong, about ·01. The plane of optic axes contains the prism axis ($c = c$); optical character, positive. The optic axial angle was measured on a section nearly perpendicular to an optic axis by the graphical method recently described by F. Becke.[*] This method is based on the difference in curvature of the black hyperbola bar which passes through the optic axis, for different optic axial angles in the diagonal position. In place of the type of revolving drawing stage described by Becke, a somewhat simpler form was devised which can be clamped directly to the microscope and can be readily adjusted to suit the conditions. This method of Becke is only an approximate one and should only be used when

[*] Becke, F., Die Messung der optischen Axen der Hyperbola-Krümmung. Tscherm. Min. petr. Mitth. xxiv, pp. 32–49, 1905.

better methods cannot be applied—a point which was realized and emphasized by Becke in the original paper. The values for the optic axial angle in air thus obtained were much lower than those given for natural enstatite, ranging between 44° and 70°,—a fact for which no explanation has yet been found. Similar low angles were also measured on the pure enstatite from the Bishopville, S. C., meteorite, which will be discussed in a later paragraph.

The specific gravity at 25° is lower than that for the monoclinic variety:

Preparation I (not entirely free from monoclinic).	Preparation II (free from monoclinic).
3·176	3·176
3·174	3·174
Average	3·175

Intergrowth of enstatite and monoclinic pyroxene.—Both from the molten silicate and from solutions of it, though only rarely from the latter, enstatite and the monoclinic form were obtained together, sometimes in parallel intergrowth. In a product of magnesium metasilicate in molten magnesium chloride and also in a preparation of amorphous silica heated with magnesium chloride, the intergrowth of the two phases was clearly marked on a section after the clinopinacoid (fig. 6). In the figure the arrows represent the positions at which the different lamellae extinguish between crossed nicols. Lamellae 1 and 3, monoclinic, are in twinning position and extinguish at an angle $c:c = 22°$; 2 extinguishes parallel and is enstatite.

FIG. 6. Intergrowths observed on (010), Enstatite—Mg-pyroxene.

On such sections the difference in refractive indices between the two forms was very slight; the birefringence of the monoclinic lamellae appeared somewhat stronger.

Parallel intergrowths of enstatite and a monoclinic pyroxene are not uncommon in nature, and although they have been frequently described, no one, apparently, has suspected that the two forms may have the same composition.

In scanning the literature on this subject, it soon became evident that natural enstatite is rarely pure magnesium silicate, but nearly always contains some ferrous silicate. The purest enstatite is probably that of the well-known Bishopville, S. C., meteorite, specimens of which are preserved in the National

Museum. Through the kindness of Prof. C. U. Shepard, the owner of these specimens, and the courtesy of Dr. G. P. Merrill, the writers obtained ·75 gr. of this material, which, on microscopic examination, proved to contain not only enstatite but also occasional intercalated lamellae of monoclinic pyroxene identical in its optical properties with our artificial monoclinic variety. The Bishopville enstatite was analyzed by J. Lawrence Smith[*] and shown to be almost pure magnesium metasilicate. On this enstatite the following properties were determined : cleavage 110 good ; $\gamma = 1·658 \pm ·003$, $\beta = 1·653 \pm ·003$, $a = 1·650 \pm ·003$ (by Schroeder van der Kolk's method of refractive liquids) ; $c = c$; optic axial angle $2\text{-}V = 31°$, average of six determinations on different sections nearly normal to an optic axis by the graphical method of Becke ; optical character, positive. The refractive indices of the interbanded monoclinic lamellae were very close to those of the enstatite and extinguished at an angle $c : c = 21°·6$, an average of 10 measurements on two different sections.

Dr. G. P. Merrill has called the attention of the writers to the fact that in his experience the pyroxenes of meteorites often show extinction angles much too low for augite or diopside, and are, moreover, very frequently twinned polysynthetically after the orthopinacoid. Time has not permitted an extensive microscopic examination of natural intergrowths of enstatite and monoclinic pyroxene to test the above inference, but the conclusion seems reasonable that not only those of meteorites but those of rocks also, which are not uncommon, are likewise aggregates of two polymorphs, and do not, as generally believed, contain diopside or augite.

The Transformation of Enstatite into Monoclinic Pyroxene.—When heated to high temperatures, enstatite passes over very slowly into monoclinic pyroxene, the time required depending mainly upon the temperature, as will be readily seen from the table below.

TABLE V.

Change of Enstatite into Monoclinic Pyroxene at Different Temperatures.

Time.	Temperature.	Change.
1 day	1200°	None detected.
2 days	1250	" "
22 hours	1260 −1280°	Slight if any.
3 days	1260 −1290	Probably some change.
18 hours	1335 −1350	None detected.
17 hours	1365 −1415	Evident change.
5 hours	1440 −1460	Much change.
20 minutes	1500 max.	Apparently complete.

[*] This Journal (2), xxxviii, p. 225, 1864.

The above data show that in a few days time the change is
first apparent between 1260° and 1290°, and that it is here
extremely slow. Comparing this table with the one on p. 399,
it is clear that the glass crystallizes directly to monoclinic
pyroxene about 100° lower. By the use of a solvent, the same
change proceeds as low as 800° and probably even lower.
Calcium vanadate, or still better, magnesium chloride, under
the conditions described on p. 389, yields well-shaped crystals of
the monoclinic variety at 800°.

The natural enstatite of the Bishopville meteorite showed
an identical behavior when heated to 1450°; the enstatite with
its parallel extinction disappeared completely and was replaced
by the twinned monoclinic lamellae, the latter still preserving
the original prismatic direction of the enstatite and also appar-
ently the cleavage, the size of grain of the two phases being
about the same and the original outline of the enstatite frag-
ments being still preserved after the paramorphic change. A
specimen of enstatite from Webster County, North Carolina,*
containing ferrous silicate also passed into the more stable
monoclinic form when it was heated. Here magnetite was
observed as a by-product.

III. *Monoclinic Amphibole.*—In several of our prepara-
tions of magnesium silicate which had been crystallized by
more or less rapid cooling, small quantities of a twinned
monoclinic form were observed, whose properties, with the
exception of the extinction angle, were similar to those of the
orthorhombic amphibole (the fourth form which is described
under IV). Later, in studying the action of water on the lat-
ter substance at 375°–475°, we observed the constant recur-
rence of this monoclinic amphibole in larger amounts than in
the original preparations; when, however, the amphibole was
heated alone to considerably higher temperatures (above 900°)
no such transformation took place. The change with water
was always quite incomplete, but further experiments, it is
hoped, may point the way to satisfactory conditions of forma-
tion.

Properties of Monoclinic Amphibole.—The crystallites of
the monoclinic magnesian amphibole were invariably micro-
scopic in size and too small to admit of a satisfactory study of
their optical constants. Their direction of elongation is the
prism axis, with which they extinguish at a small angle. In
polysynthetically twinned fragments, a maximum extinction
angle $c:c = 11°$ was observed, though smaller angles, 4°–8°,
were noticed more frequently. The average refractive index

* The writers are indebted to Dr. G. P. Merrill of the National Museum
for these specimens.

is very nearly equal to that of the orthorhombic amphibole ($\beta = 1.585$), while the birefringence is not strong and is of the same order of magnitude as that of the orthorhombic form. The crystals, like those of the orthorhombic amphibole, are not so clear and transparent as the higher refracting pyroxenes, often showing distinct lines of growth; the twinning lamellae are usually fine and less sharply defined than in the monoclinic pyroxene. Intergrowths of the orthorhombic and monoclinic amphiboles were also observed occasionally, though they were distinguished with less certainty than in the pyroxenes.

The change of the orthorhombic to the monoclinic amphibole with water at temperatures of 375°–475° did not yield any well-formed crystals; the product appeared to be rather the result of a paramorphic change in the solid state. In the hope of getting individually developed crystals, we attempted the synthesis of this form from magnesium salts and soluble silicates or silica, and succeeded in getting a product with optical properties similar to those of the magnesian amphiboles, but in fibers so small that it was impossible to say whether they were orthorhombic or monoclinic. In view, however, of the partial change of the former into the latter, it seems probable that they were monoclinic.

Experiments in the Synthesis of the Amphibole at Low Temperatures.—Chrustschoff, some years ago, published a description of a method for the formation of hornblende in which a mixture of silicic acid, alumina, lime, magnesia, ferrous and ferric oxides, and the alkalies, partly in solution, partly precipitated, were heated in sealed glass vessels at a temperature of 550° for three months.*

It seems to us that glass vessels of such extraordinary properties deserve to be better known, and that the experimenter should have given some details concerning them, especially where they can be obtained, together with some information about his temperature measurements.

The experiments which we shall describe were done in a steel bomb 16^{cm} long, 2·7^{cm} internal diameter, and 1·4^{cm} thick, which was made by boring out a piece of steel shafting. The bomb was closed by a plug also of steel having a total length of 8^{cm}, the screw of which was 4^{cm} in length and fitted into a thread cut in the end of the bomb. A tight joint was insured by a washer of annealed copper 3 or 4^{mm} thick. The steel surfaces in contact with it were planed smooth, and into each were cut a number of very narrow concentric grooves about half a millimeter deep. To close the bomb, the plug was

* Comptes Rendus, cxii, p. 677, 1891.

screwed in by a long heavy wrench until the copper filled the grooves. A new washer should be used for each experiment. The capacity of the bomb was great enough to admit a cylindrical platinum crucible holding about 30^{cc}. Temperature measurements were made by introducing an insulated thermo-element into a 7^{mm} hole in the plug, the end of which it reached within 5^{mm}. The source of heat was a Bunsen burner. To distribute the heat more evenly, the bomb was surrounded by a collar of asbestos and sheet iron with a hole on the under side through which the flame passed. The joint was shielded from the latter by an annular asbestos disk which was slipped over it.

For the synthesis of the amphibole, the magnesium was taken in soluble form, either magnesium-ammonium chloride or a mixture of magnesium chloride with a sodium bicarbonate solution; while the silica was used in the amorphous state or in combination as sodium metasilicate. Generally ·25 or ·50 gram of magnesia was dissolved in the equivalent quantity of hydrochloric acid, then the ammonium chloride or sodium bicarbonate was added, and finally the silica or sodium silicate. This mixture was poured into the platinum crucible with 25^{cc} or more of water, covered, and put into the bomb, which was then closed tight and heated from 3 to 6 days at temperatures ranging from 375° to 475°. Although in the course of these experiments the details were varied considerably, we were only able to ascertain that the products formed at the higher temperatures were usually better crystallized.

When the bomb was opened, it generally contained more or less water, sometimes several cc.; the inner wall of the bomb itself was coated with magnetite, and sometimes the platinum crucible was covered with beautiful octahedra of the same mineral. In some experiments in which the water was nearly all gone, the bomb showed when cold an internal pressure and the odor of ammonia was noticeable.

After removal from the bomb, the products were washed and dried. To the naked eye they were all much alike; they were white, and of a tough and spongy texture. Optically they left much to be desired.

They were mostly crystalline but invariably fine-grained, often cryptocrystalline, and had to be studied rather in the aggregate than in individual fibers. In all these preparations the substance present in predominant quantity consisted of complex groups of fibers which extinguished parallel to their elongation, this direction being that of the least ellipsoidal axis c; their refractive index was less than 1·60 and agreed with that of the magnesium amphibole, so far as such minute fibers admit of measurement. The birefringence was low.

In addition to this substance small amounts of both the orthosilicate and quartz were observed. The crystals of the former were frequently well developed and exhibited the characteristic crystal habit of fosterite ; they extinguished parallel to the prism edge, had an average refractive index of about 1·66, and much stronger birefringence than either the metasilicate or quartz.

The quartz crystals were ordinarily very small and recognizable only by their refractive index. In one preparation, however, where the sodium silicate in the form of large lumps was heated with magnesium ammonium chloride for 3 days at 400°–450°, numerous quartz crystals were found, the longest of which measured nearly 3^{mm}. They were water-clear, doubly terminated, sharply defined crystallographically, and resembled crystals of the natural mineral. Both optical and crystallographic measurements were made on these crystals, the results of which have been described at length in another paper[*] on the minerals of the lime-silica series.

In the products much of the material was too fine even for approximate determinations and may have contained other substances than the three cited above. It is noteworthy, however, that the pyroxene form of the metasilicate was not produced, but apparently the low refracting amphibole.

IV.—*Orthorhombic Amphibole. Kupfferite.*[†]—If magnesium silicate be melted and cooled without any special precautions, there may usually be detected, under the microscope, in the crystallized product, patches of a substance which differs markedly in appearance from either of the forms I and II. The fact that it occurred more frequently in the outer zones of the mass near the walls of the crucible, led to the suspicion that rapid cooling favored its formation. Experience soon proved the correctness of this conjecture. After a very considerable amount of work on the conditions necessary for its formation, we find (1) that the mass must be cooled rapidly, but not so rapidly as to form glass ; and that (2) for this reason, probably, the quantity of material must not be too large. A satisfactory rate of cooling is attained if a platinum crucible containing 15 or 20 grms. of the molten silicate is quickly drawn from the furnace and held, uncovered, by the operator until crystallization is complete. If the hot crucible be set at once on a tile,

[*] Day, Shepherd and Wright, The Lime-Silica Series of Minerals, this Journal, xxii, Oct., 1906.

[†] The name Kupfferite was applied originally to the natural monoclinic amphibole of this composition. In the course of time, however, the name has been shifted to designate the orthorhombic form of the same composition and like enstatite represents the pure magnesium member of the amphibole series kupfferite-anthophyllite. Hintze, however, objects to this change. Compare, Hintze, Handbuch d. Mineralogie, Bd. II, p. 1196, and E. S. Dana, System of Mineralogy, p. 384–385, 1900.

the cooling is less rapid and the monoclinic pyroxene and enstatite are more likely to form. In the above way we succeeded in one instance in crystallizing 27 grams of the silicate entirely to amphibole. Ordinarily, however, a charge of this weight cannot be cooled with sufficient rapidity to prevent crystallization of more stable forms.

Our observations appear to have established the fact that the amphibole is more likely to crystallize from the melt if the initial temperature is much above the melting point. The experiments were made in a Fletcher furnace and temperatures were roughly measured by means of a thermoelement placed under the hood where the combustion gases emerge. Only rough relative measurements were necessary. The variation in the crystalline product with the initial temperature to which the charge is heated before cooling, is given in the following table :

TABLE VI.

Influence of the Initial Temperature of the Liquid on the Product of Crystallization.

Temperature in the top of the Fletcher furnace.	Charge.	Product obtained.
1430°	6 gr.	Silicate not melted.
1470	50 "	Just begins to melt.
1470	18 "	Charge had just begun to melt.
1480	6 "	Amphibole.
1485	6 "	Monoclinic pyroxene.
1490	6 "	" "
1500	6 "	" "
1500	6 "	" "
1500	6 "	" "
1500 −1510°	6 "	Amphibole.
1510	27 "	"
1520	50 "	Monoclinic pyroxene.
1525	8 "	Amphibole.
1530	6 "	"
1530	8 "	"
1530	12 "	Delay in removing the cover about three-fourths amphibole; one-fourth monoclinic.
1530	18 "	Amphibole and a little glass.
1535	6 "	Amphibole.
1535	6 "	"
1540	12 "	Amphibole and a little glass.
1545	12 "	Amphibole.

Tollens[*] found that the unstable form of monochloracetic acid crystallized with greater certainty if the liquid was first

[*] Tollens, Chem. Ber., xvii, i, 664, 1884.

raised considerably above the melting point, and Lehmann[*] states that benzyl-phenyl-nitrosamine also yields an unstable form when *strongly heated* and very rapidly cooled.

We have proved that (pp. 402 and 411), all other forms of magnesium silicate change into the monoclinic pyroxene before the melting point is reached. If the crystal structure depends on crystal particles or units which consist of regularly arranged chemical molecules, it is not impossible that some of these groups might preserve their identity some time after fusion of the substance, and become completely disintegrated only after some lapse of time or at a higher temperature. The favorable influence of a high initial temperature on the formation of amphibole would then be due to the complete breaking down of nuclei which condition the crystallization of the monoclinic form.[†]

We tried the effect of dropping small portions of the solid amphibole into the undercooled liquid in order that they might serve as nuclei for crystallization, but the experiment did not succeed. The silicate liquids are so viscous that the nuclei do not seem to exert any influence on the crystallization. The negative effect of nuclei is very strikingly brought out in the following way: Magnesium silicate can be chilled in such a manner as to yield radial spherulites of monoclinic pyroxene embedded in glass. Now when this cake is heated again at 900°, not only do the existing nuclei fail to grow, but they exercise no orienting influence on the new crystals which form.

As this substance has not been obtained before, some further details regarding its crystallization may be of interest. It usually begins on the upper surface of the melt next to the walls of the crucible, forming a fringe of converging fibers which grow toward the center, though sometimes a number of rather widely separated nuclei start at points on the upper or lower surface. This crystal form is characterized by a considerably slower growth than the monoclinic. If, in a crucible in which the amphibole has already begun to crystallize, the still liquid portion be touched by a wire, the disturbance is instantly followed by the appearance of a monoclinic nucleus. The difference in the rate of growth of the two crystal forms is then very striking. We early noticed a very marked difference in the rise of temperature during the crystallization of these two forms, the monoclinic raising the temperature to a dazzling white; and though the difference must be partly due

[*] O. Lehmann, Molekularphysik, vol. i, p. 211.

[†] A similar conception has been advanced in a paper by Day and Allen to explain the superheating of the alkaline feldspars. This Journal, series (4), xix, p. 124, 1905.

to the rapidity of the process, we were led to suspect what afterwards proved true, that the amphibole would pass over into the other with evolution of heat. This and the method of its formation by sudden cooling are characteristic of monotropic forms.

Interesting results were obtained in an attempt to measure the approximate temperature at which the amphibole crystallizes. As a determination of a physical constant the attempt failed, because the disturbance caused by touching the liquid with the element was sufficient to start the crystallization of the monoclinic form in every instance. The following trials were made with the bare thermoelement dipped directly into the liquid, which above 1100° is easily penetrable with a wire.

Experiment 1.—As soon as crystallization began, the element was dipped into the center of the charge. Temperature 1350°. All monoclinic pyroxene.

Experiment 2.—Amphibole started to crystallize in the outer zone. Measurement as in 1. Temperature 1300°. Monoclinic pyroxene started at once.

Experiment 3.—Same as 2. Temperature 1300°.

Experiment 4.—Amphibole began to crystallize on the upper surface next the crucible wall as in 2. The element was dipped in, on the boundary line, between solid and liquid, about 1^{cm} from the crucible wall. Temperature 1150°. Monoclinic pyroxene started instantly.

Experiment 5.—Amphibole began to crystallize as usual. We waited until it nearly covered the surface and then dipped the element into the liquid, which remained in the middle. Temperature 1180°. When the charge was removed from the crucible, all but the upper layer proved to be monoclinic pyroxene.

Experiment 6.—Like Experiment 4. Temperature 1165°.

The rise of temperature with crystallization, the rapid radiation of heat from an unprotected crucible, the variation of temperature in different parts of the mass, all prevent anything better than rough temperature estimates, but the fact that the amphibole forms in a region near which a slight disturbance is sufficient to crystallize the glass to monoclinic pyroxene, is conspicuous and important. This temperature has been shown in an earlier part of the paper to be above 1150°.

Properties of Orthorhombic Amphibole.—This amphibole appears white and porcelain-like, and crystallizes in radial spherulites and fibrous aggregates. Since we have not yet been able to obtain crystals suitable for measurement, its identification rests solely on the correlation of its other properties, chiefly optical, with those of the natural mineral, kupfferite.

The fibers were too fine and too intimately intergrown to

show the cleavage plainly, still in a number of cases where fibers were tilted to a vertical position under the microscope an indistinct cleavage of about 120° was observed. Their hardness is 6. In transmitted light the aggregates do not appear so clear and transparent as the pyroxenes, but are usually of a pale brown color. The refractive indices were measured by the method of refractive liquids : $\gamma = 1 \cdot 591 \pm \cdot 003$, $a = 1 \cdot 578 \pm \cdot 003$, $\beta = 1 \cdot 585 \pm \cdot 004$. Birefringence is not strong, ·013 approximately, and the interference colors are confined to the bright tints of the first and second orders. The extinction is usually parallel to the direction of elongation, although in a few sections a small extinction angle, $c : c = 3° - 6°$, was observed, indicating intergrowths of orthorhombic and monoclinic amphiboles similar to those observed in nature. The plane of the optic axes lies parallel to the long direction ; the optic axial angle is large and the optical character apparently positive, determined on a section nearly perpendicular to an optic axis. The pleochroism is $c =$ brown, and b lighter brown ; absorption, $c > b$.

Lines of growth are often distinct within the crystallites and exhibit a plumose arrangement.

Although the above optical data do not suffice to prove definitely that this form of magnesium metasilicate is an amphibole, they do agree closely with the properties of the orthorhombic amphibole of similar composition found in nature. Unfortunately, the definite solution of this question must be deferred until after means have been devised to produce measurable crystals.

The specific gravity was determined on several different preparations, two of which (I and II) were very carefully examined microscopically and found to be practically pure ; the third, having been observed by the same method to contain small quantities of glass and the monoclinic form, was separated with great care by heavy solutions (methylene iodide and benzene), the separation of each portion being twice repeated and controlled by the microscope.

<div align="center">Specific gravity at 25° C.</div>

Prep. I.	2·858	Prep. II.	2·860	Prep. III.	2·855
	2·856		2·860		2·853
	2·857		2·860		2·854
Average,					2·857

Transformation of Orthorhombic Amphibole by Heat.— The orthorhombic amphibole changes, like enstatite, and somewhat more rapidly, into the monoclinic pyroxene, when heated to a sufficient temperature. Here, too, the change is sluggish, as the following table indicates :

TABLE VII.

Change of Orthorhombic Amphibole to Monoclinic Pyroxene.

Time.	Temperature.	Observations.
1 day	1020°–1040°	No change.
2 days	1055 –1077	Indications of slight change.
20 hours	1100 –1100	No change observed.
18 hours	1120 –1140	Fragments dotted with pyroxene.
3 days	1127 –1153	All changed.
18 hours	1144 –1173	Partly changed.
2 days	1150 –1183	All changed.

It is possible that at the lower temperatures the amphibole passes into enstatite; the product is there so fine-grained that a microscopic distinction between the two pyroxenes cannot be made.

PART II.—RELATIONS OF THE DIFFERENT FORMS TO ONE ANOTHER.

Stability relations.—The four forms of magnesium silicate having thus been prepared and studied in detail, the question of their relative stability arises. It is well known that a substance chemically homogeneous may exist in several different physical forms, which are called polymorphic when they yield identical liquids, solutions and vapors, in which case their chemical molecules, in distinction from those of isomers, are identical. Polymorphic substances are enantiotropic when, by heating, one form changes without melting into the other at a definite temperature called the inversion point, and on cooling again the reverse change takes place. In this case, the first form is stable below the inversion point only, the second above it. The form stable at lower temperatures inverts to the other with absorption of heat, and the reverse change takes place with evolution of heat.* An instance of the enantiotropic relation is the mineral wollastonite, which inverts at about 1190°, with absorption of heat, into a second form, pseudo-hexagonal in symmetry.

In another class of polymorphic substances there is no such inversion point, and one of the forms is more stable than the other at all temperatures below the melting point. These relations are best expressed by diagrams.

* Given the relations of the vapor pressures, this follows from the second law of thermodynamics. Van't Hoff, Vorlesungen über Theoret. u. Phys. Chemie, Braunschweig, 1901, ii, 128.

Enantiotropy.—In fig. 7,

OT = axis of temperatures.
OP = axis of vapor pressures.
abc = vapor tension curve of liquid.
ed = vapor tension of solid stable below T_2.
db = vapor tension of solid stable above T_2.
T_2 = inversion point.
T_1 = melting point of form stable above T_2.
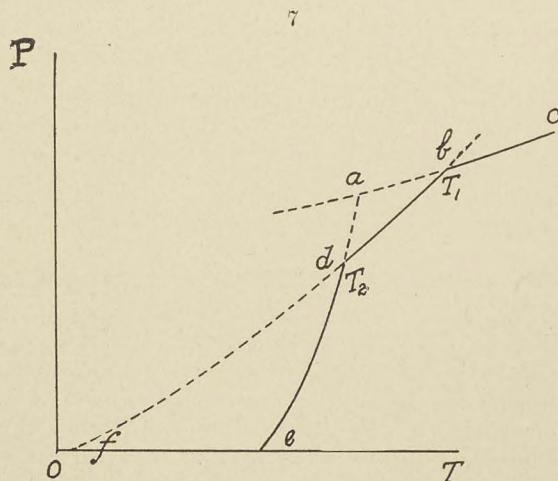
Fig. 7.   Vapor pressure curves in a case of enantiotropy ; *ed* is curve of solid stable below T_2 ; *db* is curve of solid stable above T_2.   The full lines represent a condition of stability, the dotted lines a condition of instability.

The two curves *ed* and *fb* intersect at *d* below the melting point curve.   At this point the two forms have the same vapor pressure, and are therefore in equilibrium, and the temperature, T_2, is the inversion point.   Likewise, the point T_1 is common to two curves, *bd* of the solid stable at higher temperatures, and *ac* of the liquid ; at that point, therefore, this solid and the liquid are in equilibrium, and T_1 is the melting point.   Since in general the curve *ed* cannot be prolonged so as to intersect with the curve *ac*, the solid stable at lower temperature usually has no melting point.   *bd* can usually be prolonged to low temperatures by sudden cooling or otherwise, a fortunate circumstance without which nearly all physical and chemical data upon the solids stable only at high temperatures would be unattainable.

Monotropy.—In fig. 8,

> OT $=$ axis of temperatures.
> OP $=$ axis of vapor pressures.
> abcd $=$ vapor pressure curve of liquid.
> eb $=$ vapor pressure curve of unstable solid.
> fc $=$ vapor pressure curve of stable solid.
> T$_1$ $=$ melting point of stable form.
> T$_2$ $=$ melting point of unstable form.

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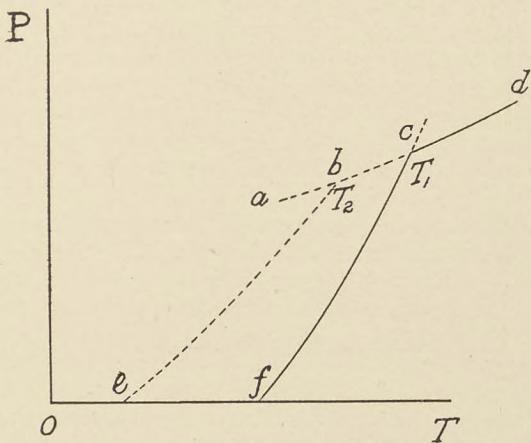
FIG. 8.   Vapor pressure curves in a case of monotropy; *eb* is curve for unstable form; *fc* is curve for stable form.

This figure represents the relations between the vapor pressure curves of two monotropic solids and their corresponding liquid. The curve differs from the preceding case only in that *fb* and *ed* do not intersect before reaching the melting point curve *abc*. At *b* the vapor pressure of one solid is equal to that of the liquid, and the two are in equilibrium; T$_2$ is therefore the melting point of this form. Similarly, T$_1$ is the melting point of the second (stable) solid. It will be noted that for a given temperature the vapor pressure of the first solid is always greater than that of the second; the two curves do not intersect below either melting point and therefore are not in equilibrium at any temperature; the solid of lower vapor pressure is more stable than the first throughout. The melting point of the unstable solid is always lower than the other, but in practice the unstable form often changes into the more stable before its own melting point (T$_2$) is reached.

Although many solids, like the minerals under discussion, have a vapor tension much too low for measurement at these temperatures, the relations are as represented in the diagram.*

The stability relations of the four polymorphic forms of magnesium silicate may be shown in the same way by a simple diagram (fig. 9). These curves do not, of course, represent measured vapor pressures, but simply the order of the stability

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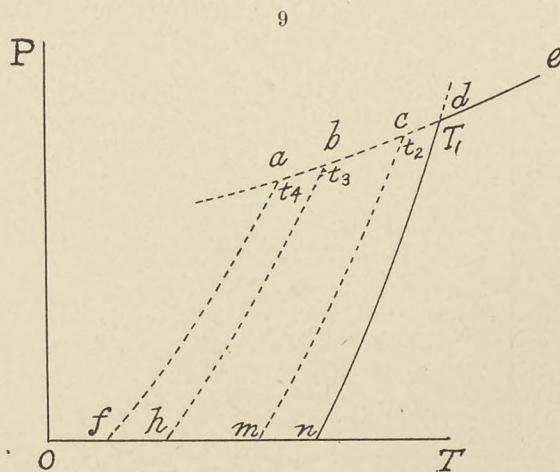
FIG. 9. *fa* is vapor pressure curve for orthorhombic amphibole; *hb* is vapor pressure curve for monoclinic amphibole; *mc* is vapor pressure curve for orthorhombic pyroxene; *nd* is vapor pressure curve for monoclinic pyroxene.

of the forms. As is proved by the experiments described below, the monoclinic pyroxene, at atmospheric pressure, is the most stable, and the others bear a monotropic relation to it, their relative stability being in the order indicated by the vapor pressure curves.

Two lines of evidence lead to this conclusion : (1) *a*. Enstatite and the amphiboles, while still in the solid state, pass over at high temperatures into monoclinic pyroxene which cannot be changed back without passing through the amorphous state ; *b*. At much lower temperatures (about 800°) the same three forms can be dissolved and recrystallized simultaneously into the monoclinic pyroxene by means of fluxes ; (2) enstatite and the two amphiboles change into monoclinic pyroxene with evolution of heat.

(1) Although it was shown conclusively that the amphiboles change into monoclinic pyroxene above about 1150°, and

* Roozeboom, Heterogen Gleichgewichte, Heft. 1, 158–159, Braunschweig, 1901.

enstatite changes to the same form above 1260°, and that on cooling neither of the changes is reversible, these facts in themselves do not prove monotropy. In certain cases of enantiotropy, mere cooling of the form stable at high temperatures does not suffice to revert it to the other form, even when both forms are in contact and unlimited time is allowed.* This inertia is apparently due to the great internal friction between the molecules at temperatures below the inversion point. The molecular immobility may be overcome by the use of suitable fluxes in which solution of the unstable form and precipitation of the stable go on hand in hand, the unstable form being the more soluble. Thus pseudo-wollastonite is less stable than wollastonite below the inversion point, yet it does not revert to it at lower temperatures except by the aid of proper solvents. In this case, molten calcium vanadate proved well adapted to the purpose. The pseudo-wollastonite dissolved in it and cotemporaneously wollastonite crystallized out.

Similar tests with solvents were applied to the different forms of magnesium silicate with the result, as we have already recounted in detail (pp. 387 et seq.), that from a considerable number of solvents magnesium silicate was found to pass into solution and gradually to crystallize, invariably as monoclinic pyroxene, whatever crystal form was originally taken. This indicates that at atmospheric pressure the monoclinic pyroxene is the most stable form of magnesium silicate at all temperatures between about 800° and the melting point of the monoclinic form (1521°).

(2) In order to confirm this evidence of monotropy, we sought to ascertain the direction of the heat changes, whether exothermic or endothermic, for two of the unstable forms. The method first tried was that of Frankenheim, which consists in observing at regular intervals the rise in temperature of a mass of the substance. Heat was supplied by means of the electric resistance furnace used in this laboratory, and the temperature measured by a thermoelement.† The curves thus obtained by heating the different forms are perfectly smooth, showing neither absorption nor release of heat until the melting point of the monoclinic form is reached. The fact that all forms seem to have the same melting point indicates in itself that the other forms change into the monoclinic pyroxene before melting. The change, however, is so sluggish that it proceeds throughout a temperature interval of several hundred degrees, and the heat is therefore so uniformly distributed as not to be indicated by the curve.

* See " Wollastonite and Pseudo-Wollastonite," this Journ. ser. 4, xxi, p. 95, 1906.
† Day and Allen, Phys. Rev., xix, 184.

New Method for Detecting the Direction of Sluggish Heat Changes.—A substance in which a transformation progresses so slowly that the accompanying heat change cannot be detected by the ordinary method, should show it plainly if the change could be forced to proceed with sufficient velocity. The heat change would then be concentrated and become visible on the temperature-time curve.

In changes of this character, the rate of change depends on the temperature, and increases rapidly with it. If, therefore, a substance which is unstable at high temperatures be introduced into a furnace which is several hundred degrees above the lower limit of the unstable region, the heat effect is in general easily followed. In our experiments the apparatus shown in fig. 10 proved very satisfactory for the purpose. An empty platinum crucible is first placed on a pedestal of refractory material in the electric resistance furnace. The unglazed porcelain tube, A, 1^{cm} in inside diameter and open at both ends, passes through holes drilled in the two covers, B and B′, and is then clamped in the position shown in the figure, the lower end of the tube reaching down to the top of the crucible. The thermoelement C is covered by a platinum shoe, D, which should occupy the same position in all the experiments, i. e., about the center of the charge. This is assured by clamping the tube in a fixed position and fastening the element securely to it by platinum wire. Care was taken to obtain like conditions in each experiment, especial attention being given to fitting together the parts of the furnace to obtain minimum radiation of heat, and in placing the crucible and thermoelement in the same relative position for each experiment.
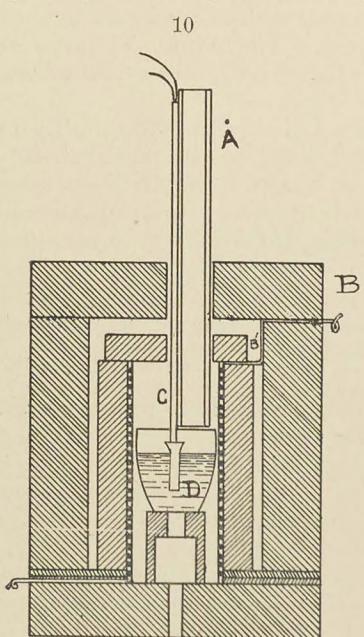
The furnace is now brought to a constant temperature, which should be sufficiently high to insure a rapid change of state. In the particular substances which we investigated, temperatures ranging from 1425°–1475° were found best adapted to show the heat effect. A weighed portion of the substance (40

or 50 grams) is then quickly dropped through the tube into the crucible, after which temperature readings are made at half-minute intervals until the temperature of the crucible again becomes practically constant.

In a second experiment under the same conditions, the product of this first change is introduced into the furnace as before, and a second temperature curve determined under exactly the same conditions. A comparison of the two curves plainly indicates the direction of the heat change. If an evolution of heat has taken place, the temperature rate is accelerated and the curve of the unstable body lies to the left and above that of the stable form, as shown in curve I of fig. 11. On the other hand, if there has been an absorption of heat, the temperature rate is retarded and the curve of the unstable form lies to the right and below that of the stable form.

In order to test the method, substances were first tried in which the direction of heat change was known, e. g., wollastonite, which passes into pseudo-wollastonite with absorption of heat ; wollastonite glass, which crystallizes with evolution of heat ; and albite, which melts with absorption of heat,— all very slow changes. Fig. 11 contains the results obtained with wollastonite and wollastonite glass. The number of curves in a single figure and their general similarity of form have made it inadvisable to confuse the figures by attempting to show the observed points on each curve. The observed electromotive forces in microvolts are therefore tabulated separately (Table VIII). The corresponding temperatures are not important, as the point which we desire to establish depends merely upon the relative displacement of that portion of the curve in which a change of state may be expected to occur. The curves II are heating curves for pseudo-wollastonite, which is the stable form at the temperatures of the experiment, and therefore suffers no change of state. Curve I, the corresponding curve for wollastonite glass, lies to the left and above the curves for pseudo-wollastonite, and plainly indicates an evolution of heat, since all other thermal conditions are identical in the two cases. The curves for wollastonite, III, lag behind those for pseudo-wollastonite, and indicate heat absorption. The results for albite and albite glass are shown in fig. 12 (Table IX). It is interesting to compare these results for albite with those obtained for orthoclase (which resembles albite very closely in its thermal properties), in a previous investigation in this laboratory by the Frankenheim method (fig. 13).*

* Arthur L. Day and E. T. Allen, "The Isomorphism and Thermal Properties of the Feldspars," this Journal, series 4, xix, 93, 1905.

11
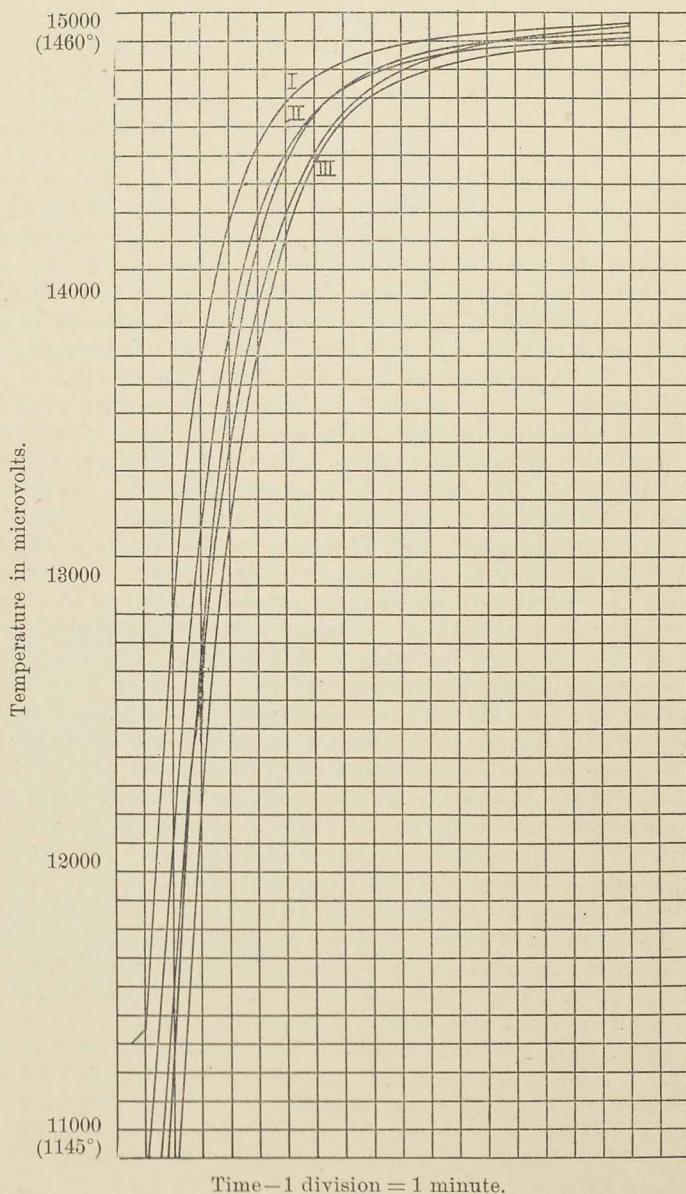

Fig. 11.   I = Wollastonite glass (one curve).
        II = Pseudo-wollastonite (two curves).
       III = Wollastonite (two curves).

12

Time — 1 division = 1 minute.
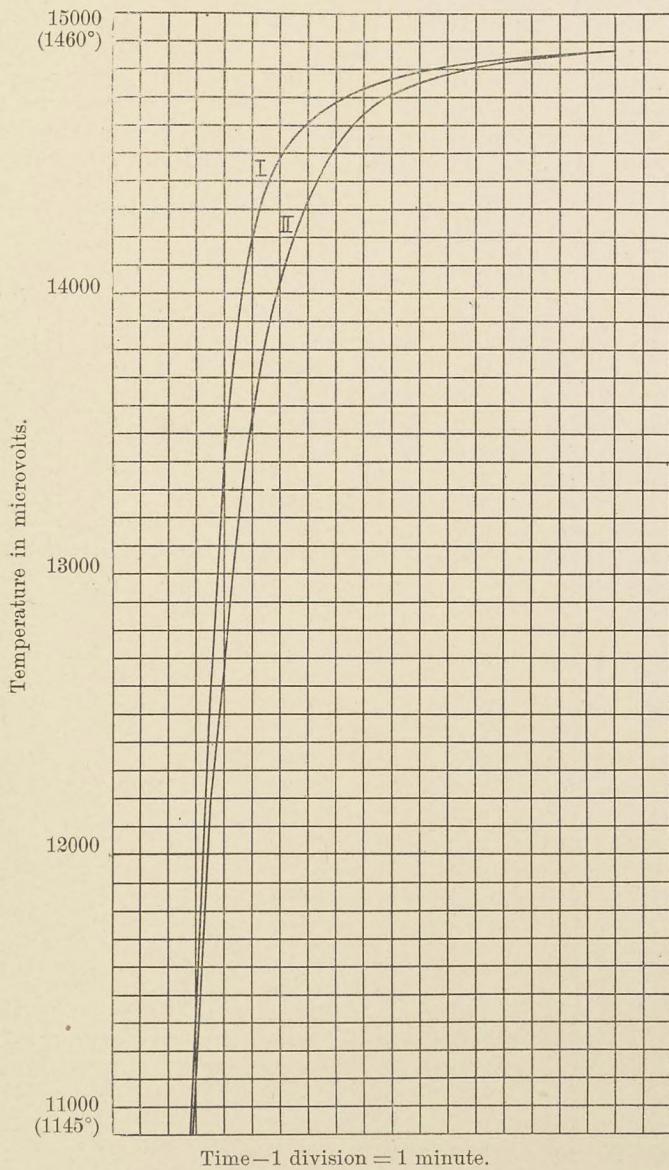
FIG. 12.   I = Albite glass.
                  II = Albite.

The curves in this figure (fig. 13) were obtained by heating large charges (about 100 grams) of orthoclase to a temperature which caused a complete change of state. During the time of melting, which, in the alkaline feldspars, extends over quite an interval, the rate at which the temperature rises is retarded by heat absorption, but the change is so slow that this retardation is very slight. The indentation in the curve is

TABLE VIII (see fig. 11).

Time.	Wollastonite glass.	Pseudo-Wollastonite.	Wollastonite.	
0 min.	15000	15000	15000	15000	15000
	11400	11300	10600	9900	11100
1 "	11450	10905	9960	9170	10380
	12210	11450	10520	9700	875
2 "	12890	12115	11350	10585	11560
	13445	734	12175	11495	12215
3 "	790	13208	790	12245	715
	14065	595	13305	12840	13160
4 "	262	880	680	13215	484
	418	14114	970	550	760
5 "	529	281	14185	818	974
	619	416	350	14050	14154
6 "	683	514	474	225	292
	732	593	570	368	414
7 "	770	650	641	473	506
	801	696	695	558	585
8 "	825	731	738	620	646
	845	761	772	670	696
9 "	861	784	798	706	736
	875	801	819	735	770
10 "	885	816	835	759	795
	895	829	850	780	818
11 "	903	840	862	798	837
	911	850	872	812	851
12 "	917	858	880	824	867
	923	865	887	835	879
13 "	927	872	893	844	889
	932	877	899	852	899
14 "	937	882	904	859	907
	940	888	908	864	915
15 "	944	891	912	869	921
	948	895	915	873	928
16 "	951	898	919	877	933
	953	901	921	880	939
17 "	956	904	924	883	945
	961	908	927	885	950
18 "	964	911	929	887	954

TABLE IX (see fig. 12).

Time.	Albite glass.	Albite.
0 min.	15000	15000
	11100	11850
1 "	9900	315
	9900	720
2 "	10525	12250
	11430	800
3 "	12365	13140
	13145	478
4 "	695	716
	14075	919
5 "	300	14080
	448	221
6 "	543	334
	610	432
7 "	659	513
	699	584
8 "	727	636
	751	676
9 "	770	705
	785	728
10 "	800	747
	811	761
11 "	821	772
	830	782
12 "	838	790
	844	797
13 "	850	803
	855	809
14 "	859	813
	864	818
15 "	868	821
	872	825
16 "	876	828
	880	831
17 "	882	834
	885	837
18 "	887	840

made evident to the eye by continuing as a dotted line the course the curve would have followed, had no absorption of heat occurred.
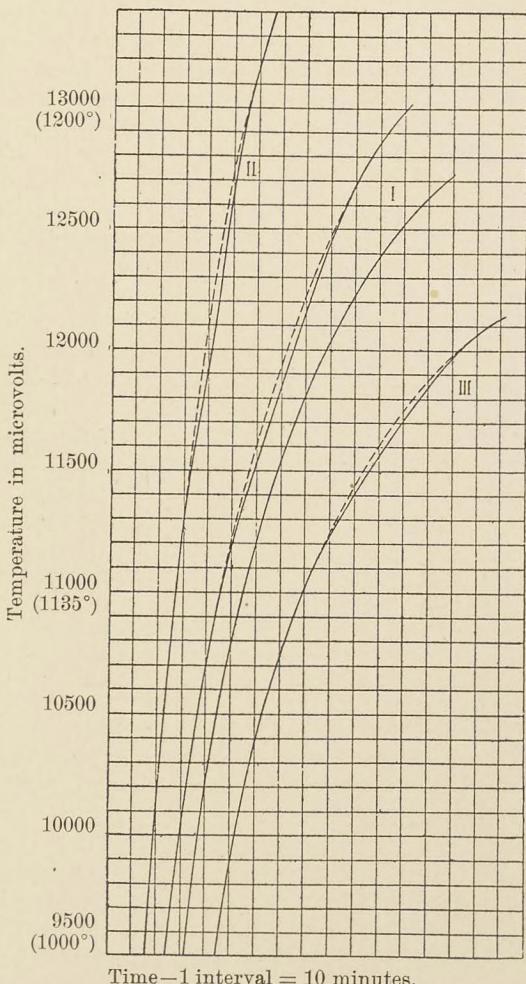
Fig. 13. Curves showing heat absorption in melting orthoclase.

Figures 14–18 (Tables X–XIV), show the curves obtained by the new method on the different forms of magnesium metasilicate. The curves for the orthorhombic amphibole, enstatite and monoclinic pyroxene in fig. 14 (Table X) were obtained in preliminary experiments, and are less accurate than those obtained in the later experiments, due to the fact that the posi-

14
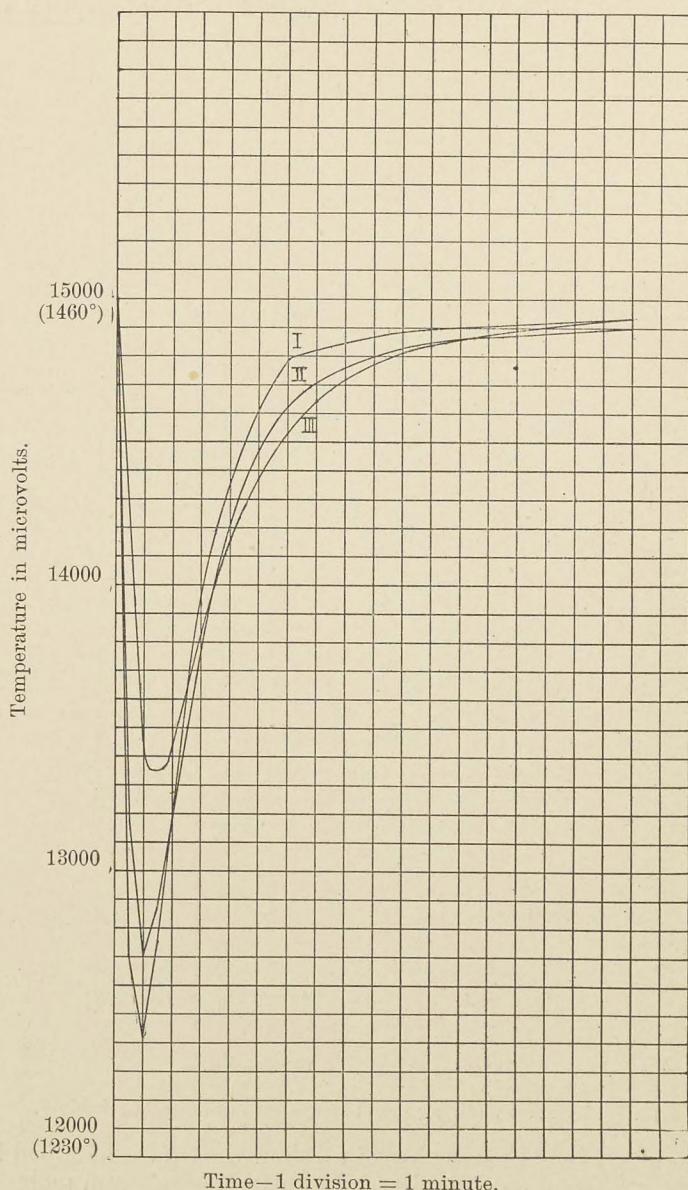
FIG. 14.   I = Orthorhombic amphibole.
            II = Enstatite.
            III = Monocline pyroxene.

15

Time—1 division = 1 minute.
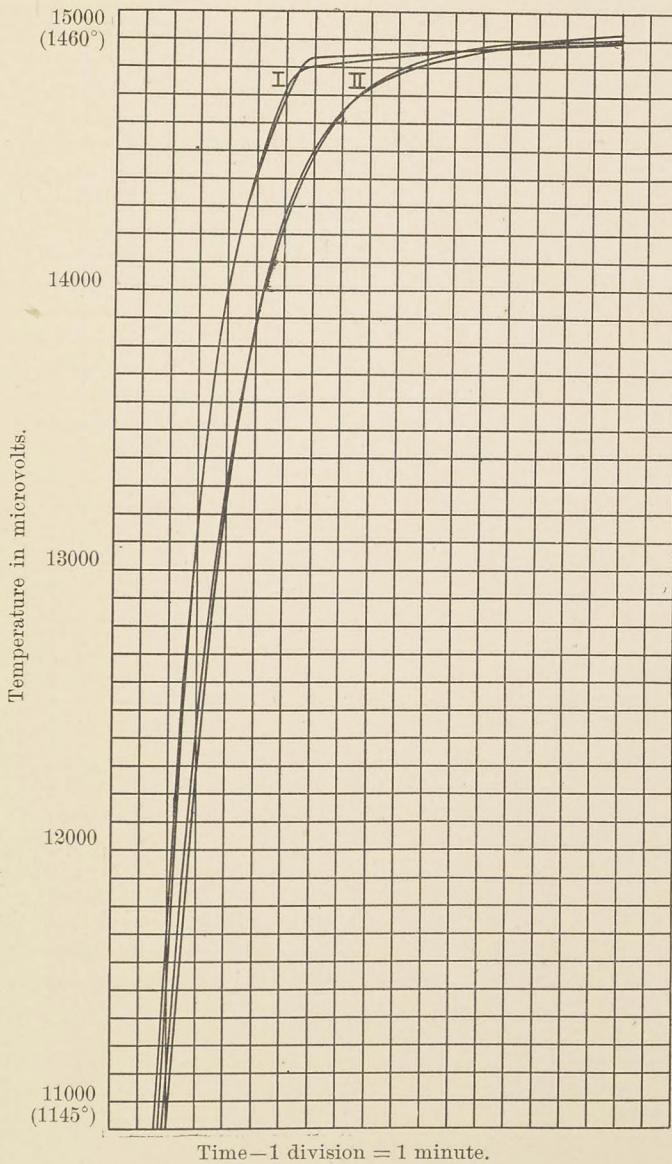
Fig. 15.   I = Orthorhombic amphibole (two curves).
            II = Monocline pyroxene (two curves).

16
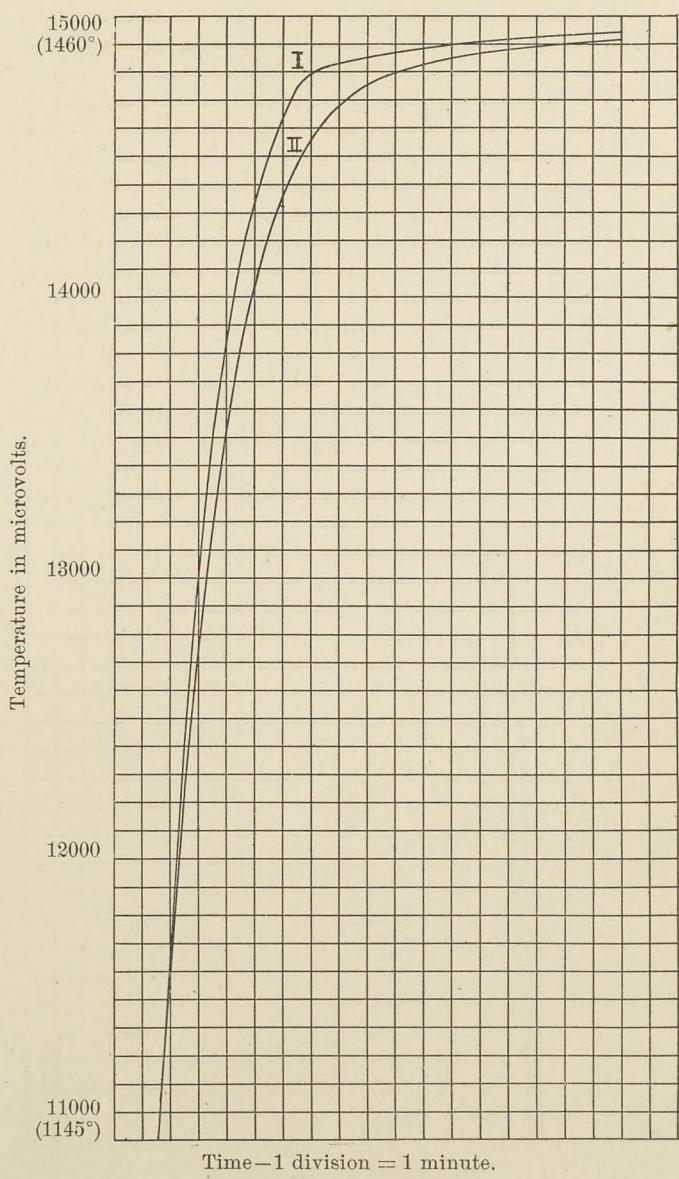
FIG. 16.   I = Orthorhombic amphibole.
            II = Monoclinic pyroxene.

17
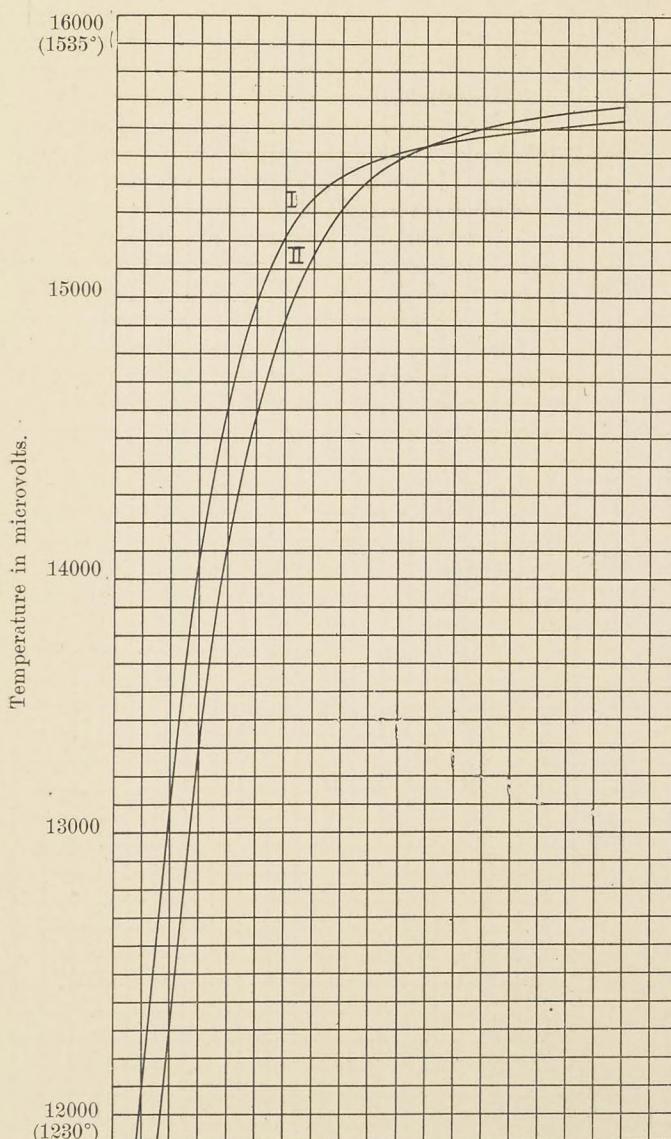
FIG. 17.   I = Enstatite.
   II = Monoclinic pyroxene.

18

Temperature in microvolts.

Time—1 division = 1 minute.
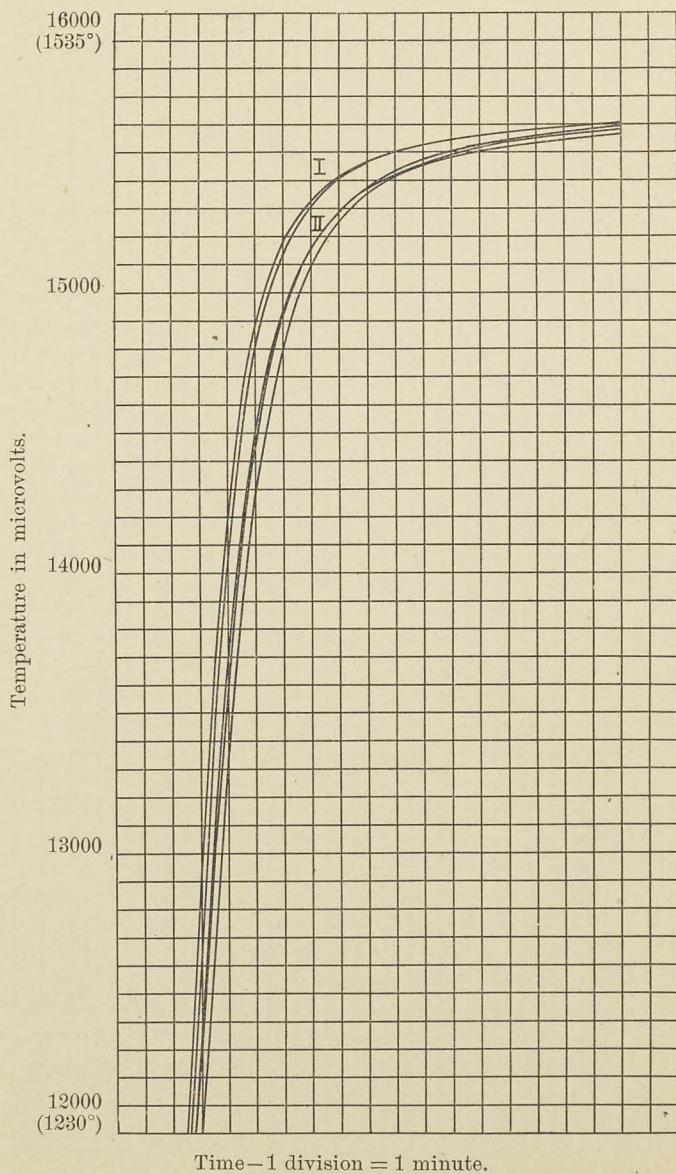
Fig. 18.   I = Enstatite (two curves).
II = Monoclinic pyroxene (three curves).

TABLE X (see fig. 14).

Time.	Monoclinic pyroxene.	Amphibole.	Enstatite.
0 min.	15000	15000	15000
		12700	13170
1 "	13500	415	12707
	350	750	870
2 "	440	13200	13175
	625	630	505
3 "	830	930	780
	14000	14180	14017
4 "	145	350	200
	265	495	353
5 "	370	600	466
	455	706	555
6 "	530	785	618
	590	803	671
7 "	640	814	708
	680	831	738
8 "	716	841	761
	745	855	781
9 "	770	869	796
	790	878	808
10 "	810	886	819
	825	876	834
11 "	837	873	847
	848	877	857
12 "	859	890	862
	869	892	864
13 "	876	894	863
	884	898	866
14 "	891	905	871
	898	910	876
15 "	903	913	881
	909	917	884
16 "	915		888
	920	923	890
17 "	926	926	893
	931		895
18 "	934	933	898

TABLE XI (see fig. 15).

Time.	Monoclinic.		Amphibole.	
0 min.	15000	15000	15000	15000
	11250	11000	10850	11050
1 "	10200	10003	9950	10200
	10520	10280	10560	770
2 "	11185	915	11530	11710
	870	11650	12460	12575
3 "	12435	12285	13120	13170
	915	830	640	655
4 "	13290	13257	980	990
	613	610	14230	14240
5 "	860	880	407	424
	14070	14100	557	585
6 "	235	266	688	716
	375	400	797	785
7 "	479	500	833	801
	566	579	839	807
8 "	630	639	839	814
	687	687	847	821
9 "	728	724	847	827
	763	755	852	832
10 "	789	778	859	838
	811	796	857	844
11 "	828	811	858	849
	843	825	862	854
12 "	855	837	865	859
	866	847	869	863
13 "	874	856	874	867
	881	865	881	870
14 "	886	871	880	874
	891	877	887	877
15 "	896	882	891	880
	903	886	893	883
16 "	908	889	895	885
	912	893	896	887
17 "	917	897	898	890
	921	901	900	892
18 "	924	904	902	894
	927			
	930			

tion of the thermoelement was less carefully adjusted, but the relative position of the curves is clearly established. Figures 15 and 16 (Tables XI and XII) contain curves for the same amphibole and monoclinic pyroxene, and figures 17 and 18 (Tables XIII and XIV) for enstatite and the monoclinic pyroxene, which represent the results of experiments made

TABLE. XII (see fig. 16).

Time.	Monoclinic pyroxene.	Amphibole.
0 min.	15000	15000
	10920	10600
1 "	343	170
	890	825
2 "	11570	11625
	12210	12380
3 "	740	995
	13180	13490
4 "	520	840
	815	14120
5 "	14040	332
	223	500
6 "	360	630
	476	739
7 "	559	795
	627	818
8 "	678	830
	720	841
9 "	751	850
	778	860
10 "	798	868
	811	876
11 "	825	884
	838	891
12 "	849	897
	857	903
13 "	863	908
	871	913
14 "	877	917
	883	921
15 "	888	924
	893	928
16 "	897	931
	905	933
17 "	909	937
	913	940
18 "	916	942

TABLE XIII (see fig. 17).

Time.	Monoclinic pyroxene.	Enstatite.
0 min.	15800	15800
	12100	12380
1 "	11160	140
	700	670
2 "	12325	13200
	940	690
3 "	13410	14065
	805	370
4 "	14115	615
	375	820
5 "	584	980
	768	15115
6 "	915	215
	15048	295
7 "	152	352
	242	394
8 "	312	428
	372	455
9 "	418	476
	458	495
10 "	489	510
	515	523
11 "	536	533
	557	543
12 "	572	551
	588	558
13 "	601	565
	612	573
14 "	623	580
	631	587
15 "	639	594
	647	600
16 "	654	606
	661	612
17 "	666	616
	672	623
18 "	678	628
		631

with all the precautions which we have prescribed. The curves for both the enstatite and the amphibole lie to the left and above that for the monoclinic pyroxene. They therefore change into the latter with evolution of heat, and hence are monotropic with respect to it. The curve for the orthorhombic amphibole lies outside that of enstatite, and consequently the exothermic change is quantitatively greater

TABLE XIV (see fig. 18).

Time.	Monoclinic pyroxene.			Enstatite.	
0 min.	15700	15700	15700	15700	15700
	8500		10100	9800	10000
1 "	8645	9520	9400	8715	9765
	9300	9915	9848	9325	10210
2 "	9930	10615	10605	10415	11035
	10905	11475	11515	11640	12010
3 "	11800	12270	12315	12620	890
	12630	13005	13075	13475	13658
4 "	13325	605	715	14065	14205
	890	14113	14170	510	615
5 "	14290	455	510	797	877
	555	228	763	15000	15055
6 "	808	915	938	135	179
	975	15052	15068	238	265
7 "	15095	152	161	308	324
	185	230	233	366	372
8 "	242	289	287	407	410
	309	337	331	443	443
9 "	357	374	365	468	462
	386	406	394	482	481
10 "	416	431	417		499
	440	453	437		511
11 "	458	471	454		523
	476	488	469		533
12 "	492	501	481		542
	504	514	492		551
13 "	514	525	503		558
	524	534	511		565
14 "	533	543	520		570
	541	551	527		575
15 "	548	558	533		579
	555	565	539		585
16 "	561	571	545		588
	567	577	550		596
17 "	572	582	555		600
	577	587	559		605
18 "	581	592	563		604
	585	597	568		

for amphibole, which indicates that it is the least stable of the three forms. As compared with the curve of wollastonite glass, the form of the (orthorhombic) amphibole curve is significant. The change of the former begins at a much lower temperature and forms a smooth curve, while the latter changes at higher temperatures and, as a result, the influence of the heat change continues until the maximum temperature is almost reached; consequently the curve shows a sharp change in direction near the top.

Although this method is purely qualitative, repeated trials on all these substances have convinced us that the relative position of the curves is invariable. No *point* of change, of course, can be found.

In the consideration of these curves the fact must not be overlooked that they include two quantities which may be independently variable, the heat of fusion or inversion and the specific heat. In general it is undoubtedly true, and therefore a justifiable assumption in this case, that latent heats are of a greater order of magnitude than specific heats. Although glasses possess higher specific heats than the solids which crystallize from them, polymorphic forms of the same substance in all probability possess similar specific heats. For the purposes here described, we are, therefore, perfectly safe in assuming that the comparisons made are independent of *differences* of specific heat in the substances experimented upon. The results obtained for albite by this method are in full accord with well established existing data, although albite, of all the substances examined, might be expected to offer difficulties from this cause. A substance exhibiting a sluggish heat change might perhaps be found in which the relative magnitude of the specific heats of it and its product, when compared with the latent heat of the change, would be such that the latter would have less influence on the form of the curve. In such a case, the method would lead to erroneous conclusions.

It goes without saying that if the change to be investigated does not take place during the time the substance is in the furnace, the method is useless. We found this true in the case of quartz. When the temperature of the furnace was held at 1560°, only about 1 per cent of the quartz was changed during the twenty minute period of experiment, even though other evidence has shown that tridymite is the stable form above a point at least as low as 800°.[*]

Order of Stability.—We have seen (pp. 402, 410 that the orthorhombic amphibole and enstatite both pass over into the monoclinic pyroxene under circumstances which point to the greater stability of the last named form ; that the heat effect which accompanies this change of state is exothermic in all cases, but quantitatively greater in the change—amphibole $\longrightarrow$ monoclinic pyroxene. The amphiboles are, therefore, less stable than enstatite, a conclusion which is substantiated not only by the greater difficulty of forming the amphiboles, but by the closer resemblance of all the properties of the two pyroxenes. The fact that the monoclinic amphibole probably forms directly from the orthorhombic amphibole in the presence of water at 375°–475°, though the orthorhombic form is all the while in

[*] Day, Shepard and Wright, loc. cit.

excess, indicates the greater stability of the former. In connection with this it should be noted that the two amphiboles resemble each other as closely as do the two pyroxenes, the monoclinic forms being the stabler in both cases. The order of stability of the four forms is represented in the diagram (p. 414).

Volume Relations.—Although theoretically there is no reason requiring it, the facts show that the specific gravities, and therefore the specific volumes, of the four forms of magnesium silicate lie in the order of their stability:

Specific gravity of glass			2·743
"	"	" orthorhombic amphibole	2 857
"	"	" monoclinic "	*
"	"	" orthorhombic pyroxene	3·175
"	"	" monoclinic "	3·192

Geological Inferences.

Conditions of Formation of Meteorites.—It has been shown above, that the monoclinic magnesian pyroxene, though not generally recognized as a mineral, does occur in nature. After it had been found to be the stablest form of magnesium metasilicate, its occurrence seemed altogether likely. An examination of the literature then developed the fact that Fouqué and Lévy had already discovered it in meteorites.† Still their proof lacked one essential point; they assumed the composition of the mineral. The optical study of the material of the Bishopville meteorite, which has been shown to be practically pure magnesium silicate,‡ supplied the missing link in the chain: a careful measurement of all its important optical constants, and a comparison of these with the constants of our monoclinic form, established the identity of the two. Fouqué and Lévy state that in some meteorites the monoclinic form, in others the enstatite, is in excess. In the Bishopville and other meteorites, this form is intergrown with enstatite. In the similar intergrowths of enstatite with a "monoclinic pyroxene" so frequently observed in rocks, it is very probable that in some cases the latter has the same composition as the enstatite.

The parallel growths of enstatite and the monoclinic pyroxene which are characteristic of meteorites, we were able to reproduce by cooling a molten mass of pure magnesium silicate at a rather rapid rate. The slower the cooling, the more of the

* The specific gravity of this form has not been determined, because the substance has not been obtained free from other forms. Its average index of refraction is very close to that of the orthorhombic amphibole, but appears to be a trifle higher, so that we assume with some degree of probability that the specific gravities of the two amphiboles are related just as those of the two pyroxenes.

† Bull. Soc. Min., iv, 279, 1881.

‡ J. Lawrence Smith, this Journal (2), xxxviii, 225, 1864.

monoclinic form is obtained; hence we conclude that the Bishop-
ville meteorite was probably cooled rather rapidly from a high
initial temperature.   The occurrence of similar intergrowths of
the same minerals in many other meteorites indicates that the
above mode of formation is a general one, though ferrous sili-
cate, which is generally present, would lower the temperature
of crystallization.

Occurrence of unstable forms of the metasilicate in nature.—
Since the monoclinic magnesian pyroxene is the stablest form,
the question naturally arises, why does it not occur more fre-
quently in nature.   The probable explanation is that the mag-
nesium silicate of nature generally crystallized from solutions
or magmas, the temperature and viscosity of which conditioned
the formation of the enstatite or amphibole.

In the foregoing, it has been proved that under atmospheric
pressure the monocline pyroxene is the most stable form of
magnesium silicate, and it has been shown how various solvents
may transform the other polymorphs into this one.   Yet it is a
very common thing for unstable forms of enantiotropic, as
well as monotropic, substances to crystallize first[*] from solu-
tion, whether we start out with a stable or unstable form, pro-
vided the solution is not in contact with the stable solid; and
in one instance, that of mercuric iodide,[†] crystals of the unsta-
ble yellow variety sometimes form even in the presence of
nuclei of the red (stable) form, though they soon pass over into
the latter.

We had already found that the unstable amphibole forms
from *water* solutions at temperatures of 375°–475°, and it
seemed worth while to make the attempt to produce enstatite as
well as the orthorhombic amphibole from *silicate* (magmatic)
solutions at higher temperature.   We used for these experiments
portions of 50 to 60 grams, the solutions consisting of magne-
sium silicate mixed with about 10 per cent of its weight of vari-
ous other substances.   The results are recounted briefly below:

1. 40 grams magnesium silicate and 5 grams of ferric oxide were
   fused in a Fletcher furnace.   The heat was then turned off
   and the crucible allowed to cool in the covered furnace in
   which, as the walls are thick, the temperature falls at such a
   moderate rate that the pure magnesium silicate crystallizes
   almost entirely in the monoclinic form.   A microscopic exam-
   ination showed that the ferric oxide had not greatly influ-
   enced the crystallization.

   * Regarding the crystallization of suphur, see Gmelin-Kraut, Handbuch
der Chemie, vol. 1, part 2, p. 155; and for similar facts about phosphorus,
see vol. 1, part 2, p. 10.   See also O. Lehmann, Molekular-Physik, vol. 1,
p. 193, for many other instances of this kind.

   † Kastle and Reed, Am. Chem. Journ., xxvii, 217, 1902.

2 42 grams of magnesium silicate and about 4 grams of labrador-
ite (Ab₁An₁) were melted and cooled under similar condi-
tions. The magnesium silicate crystallized chiefly as mono-
clinic pyroxene with some enstatite present. Small amounts
of glass, probably plagioclase glass, filled the interstices
between the pyroxene laths.

3. To solution 1, 5 grams of orthoclase were added; the whole
was then fused and crystallized as before. This time a quan-
tity of coarsely crystalline enstatite was produced. The ortho-
clase remained as glass.

4. 50 grams of magnesium silicate and 5 grams of albite were
fused and cooled as before. The magnesium silicate crystal-
lized mostly as enstatite, with the characteristic properties:
paralled extinction, $c = c$, cleavage prismatic with an angle
of about 90°, birefringence not strong, optically positive; 2E
apparently larger than usual. The section consisted of clear
enstatite laths and intercalated patches of a cryptocrystal-
line, dust-like aggregate which appears to contain albite
and enstatite—perhaps a eutectic mixture of the two. Parts
of the aggregate had a refractive index apparently equal to
that of albite.

5. 46 grams magnesium silicate, 4 grams sodium metasilicate, and
1 gram potassium metasilicate were fused and cooled under the
usual conditions. The cake was filled with beautiful prismatic
crystals, the longest of which was 23^{mm} in length. Most of the
magnesium silicate had crystallized as enstatite, though there
was some of the monoclinic form. The optic axial angle of the
enstatite was apparently larger than usual.

6. Preparation No. 4, consisting of the metasilicate with 10 per
cent albite, was remelted and cooled more rapidly than the
previous solutions. The product consisted chiefly of the low
refracting, orthorhombic amphibole form of the metasilicate.
Many of the fragments of the product were clearer and showed
brighter interference colors than the amphiboles; they con-
sisted of finely intergrown fibers of refractive index slightly
less than that of the amphiboles (about 1·560) which may
have been due to a solid solution of albite in the amphibole.

7. 4·6 grams of albite were added to 46 grams of the magma de-
scribed under 6, giving a solution containing about 20 per cent
as much albite as silicate of magnesium. The fusion was
cooled like 6 and the low refracting amphibole formed. The
grains were not clearly transparent and exhibited the dusty
appearance observed in the albite-enstatite mixture of pro-
duct No. 4. The refractive index and other optic properties
coincided closely with those of the magnesium amphibole
from pure melts.

Silicate solutions can probably be prepared from which the
amphibole will crystallize by a process of slow cooling such as
prevails in nature, but thus far we have not hit upon a compo-
sition which is effective.

In explaining the formation of enstatite in the above cases, the influence of temperature is doubtless of importance. When pure magnesium silicate is cooled slowly enough, i. e., when crystallization occurs at a temperature not too far below the melting point, only the stable monoclinic form is obtained; if cooled more rapidly, enstatite begins to form; still more rapidly, and we have amphibole; and finally, when we chill very suddenly, glass is the result. In all these cases, the temperature at which crystallization occurs is the lower the more rapid the cooling.

The first influence of these solvents is, therefore, no doubt, to lower the temperature at which crystallization takes place, though not all of them are equally effective; the addition of labradorite and ferric oxide makes less difference than albite, orthoclase and the alkaline silicates.

This explanation is, however, an incomplete one, otherwise why should fluxes like the vanadates of magnesium and calcium, tellurous oxide, and magnesium chloride, always give the monoclinic form even at considerably lower temperatures. Comparing these solutions with those which give rise to enstatite, we note at once that the one property which serves to distinguish the two classes is the viscosity. The monoclinic variety is obtained from thinly fluid solutions. At first sight it might appear otherwise with the vanadates, because the whole mass of silicate and vanadate from which we crystallize the silicate seems little more than pasty. The most of the mass is indeed undissolved solid, but the molten vanadates are comparatively thin and so no doubt is the solution which covers the surface of the grains of silicate and colors it yellow. The enstatite, on the other hand, was obtained from solutions which are comparatively viscous at the temperature of crystallization.

The influence which the viscosity of a solvent exerts on the transformation of unstable crystals which stand in contact with it, has been very well shown by Kastle and Reed.* The substance which they investigated was mercuric iodide, an enantiotropic substance with an inversion point at 128°. The yellow form is only stable above this point, yet below that it is always obtained from solutions whatever the solvent may be. The rate at which this form passes over into the red variety, stable at ordinary temperatures, depends on the viscosity of the solvent. Thus with certain mobile solvents like water, the transformation was complete in a very short time, while under a concentrated sugar solution the red appeared only after several days, in glycerine after two weeks, and in vaseline none appeared after a year and a half. In the case of mercuric iodide, so far as known, the unstable form always

* Loc. cit.

crystallizes no matter what the solvent, but this is not true in
many other instances. It seems entirely reasonable to expect
that if a solvent by its viscosity can hinder a transformation in
the solid state, it may also in certain cases restrain the mole-
cules in the act of crystallization from assuming the configura-
tion characteristic of the stablest structure. And we might also
expect viscosity to be especially effective where the transfor-
mation of the unstable form into the stable is effected with
comparative difficulty, as it is in the case of the magnesium
silicates. This would explain why enstatite comes out of a
viscous silicate solution at a temperature much higher than that
at which the monoclinic form is obtained from thinner solutions.
At first thought one might be inclined to regard viscosity as
directly conditioning the form of the crystal, and to look upon
the temperature as merely influencing the viscosity, but further
reflection convinces that this can not be so, for we obtained
the amphibole from aqueous solutions at 375°–475°. The
properties of aqueous solution in general, however, differ
widely from others. It is probable that those movements of
the molecule which depend directly upon temperature have a
very important influence on crystallization. Although tem-
perature and viscosity are certainly important factors in the
formation of unstable modifications, the knowledge of the sub-
ject is still insufficient, and what we have is too little systema-
tized to generalize in an entirely satisfactory way.

Formation of Amphiboles.—Regarding the formation of
forms III and IV, it seems quite beyond the bounds of proba-
bility that they should be formed in nature by the rapid cooling,
which, on a small scale, is effective. On the other hand, assuming
that these forms are really amphiboles, the formation of at
least one of them from aqueous solutions, at a temperature of
375°–475°, is consistent with recognized geological forces; at
any rate, our experiments indicate that the two amphiboles
form at lower temperatures than the pyroxenes. We are inclined
to regard the pressure in these experiments as an unessential
factor, except in so far as it is necessary to prevent the escape
of water at these temperatures, because in the first place it has
been seen that both substances (III and IV) could be obtained
without pressure, and secondly, the specific volume of these
amphiboles, as of all others, for that matter, is greater than that
of the corresponding pyroxenes. According to Le Chatelier's
principle, pressure should tend to produce the system of small-
est volume.

Relation between Pyroxenes and Amphiboles.—Though we
refrain from generalizing as yet in regard to the two great min-
eral groups, the amphiboles and the pyroxenes, we can say that
the demonstration of an irreversible (monotropic) relation
between each of the two magnesian amphiboles and the stable
pyroxenes accords with the experience of many other investi-

gators that, experimentally, amphiboles may be readily changed into pyroxenes but not pyroxenes into amphiboles.

False Equilibria in Nature.—Since these studies have shown the instability of enstatite and the amphiboles of the composition $MgSiO_3$, it may be at once inferred that not all natural minerals are stable. The occurrence of the unstable forms alone constitutes what is commonly called a metastable condition (apparent false equilibrium of Duhem), in which it is generally assumed that equilibrium may be brought about by contact with the stable phase. In another part of this paper it has been demonstrated that such a contact is inadequate, in the case of the magnesium silicates, to determine equilibrium during periods of time which are within the limits of laboratory observation.

Duhem, in his Thermodynamique et Chimie (p. 436), draws a very apt comparison between chemical and mechanical systems. The statics of both are commonly treated as if the systems were frictionless, whereas in both we have to deal with a resistance which in the former is ordinary friction, in the latter an internal friction between the molecules. Chemical systems, in the majority of cases so far studied, seem capable of reaching a true equilibrium, or at least a state which approaches it within measurable limits, but where the systems are composed of viscous liquids or more especially of solids at low temperatures, true equilibrium may not be reached even after an indefinite time, the condition finally attained being not alone the result of molecular forces as conditioned by temperature and pressure, but of these retarding forces which offer an internal resistance of by no means negligible magnitude. (Duhem's genuine false equilibria.) We find in nature false equilibria of this kind, e. g., intergrowths of pyrite and marcasite* among the sulphides, and among the silicates intergrowths of sillimanite and andalusite, and enstatite with monoclinic pyroxene.† It has been generally supposed that the monoclinic pyroxene in the last-named case was a diopside, but our experiments show that similar aggregates form in artificial systems which contain no calcium and that they exist in the Bishopville meteorite. In some cases it is not at all impossible that these systems are in process of very slow change, but there is no optical evidence that this is true of the above-mentioned silicates; in other cases it may be that the two forms were deposited at different times, though in some it would appear that they were actually crystallized together; the important fact to note in them all is that they are systems which are not in equilibrium. Because a rock or mineral aggre-

* Stokes, H. N., U. S. Geol. Survey, Bull. 186.
† We have also obtained intergrowths of the two magnesian amphiboles. Therefore the aggregates of monoclinic and orthorhombic amphiboles in nature probably form another example of this principle.

gate is found in nature, therefore, where it might be supposed
to have had sufficient time for attaining equilibrium, is not a
sufficient reason for assuming that it has actually reached the
state of greatest stability.

Summary.

1. There are four crystal forms of magnesium metasilicate:
(I) a monoclinic pyroxene, having the characteristic prismatic
cleavage (92° and 88°), and a similar axial ratio $a : b$, but a ratio
$c : a$, which varies widely from that of the pyroxenes; (II) an
orthorhombic pyroxene identical with enstatite and optically
very similar to (I); (III) a monoclinic modification correspond-
ing to an amphibole in its optical properties; (IV) an ortho-
rhombic form, optically also an amphibole and resembling (III)
very closely.   These forms, with the exception of (III), have
been prepared in pure condition or with only traces of other
forms; their optical properties have been studied, their specific
gravities have been determined, their behavior on heating has
been investigated, and, in the case of (I), measurable crystals
have been obtained.

Forms (I) and (II) occur in nature, usually in mixed crystals
with ferrous silicate, and it is quite probable that the same is
true of (III) and (IV).

2. (I) is formed in pure condition by crystallizing a melt a
little below the melting point (1521°), which may be readily
accomplished by cooling slowly.   Measurable crystals are
obtained by heating any form of the metasilicate to about 1000°
in molten magnesium chloride traversed by a stream of dry
hydrochloric acid gas.   Calcium vanadate, magnesium vanadate,
magnesium tellurite, and other fluxes yield crystals which are
not so well developed.   All the other forms of magnesium
silicate pass into (I) at temperatures between 1150° and 1300°,
depending on the crystal form taken.   (II). This form (ensta-
tite) crystallizes at lower temperatures than (I); the purest prep-
aration, containing only traces of other forms, is made by heat-
ing the glass of the same composition at a temperature between
1000° and 1100°; large crystals of enstatite (up to 23^{mm} in
length) were obtained in silicate (magmatic) solutions.   (III)
forms in very small quantities by rapidly cooling the melt; there
is also evidence that it forms from (IV) when the latter is heated
with water in a bomb to a temperature of 375°–475°.   When
an aqueous solution of magnesium-ammonium chloride, or
magnesium chloride and sodium bicarbonate is heated with
amorphous silica or sodium silicate, this substance is probably
formed, though the crystal fibers are too small to decide whether
the product is identical with (III) or with (IV).   (IV) is obtained
by heating the molten silicate high above the melting point, say
to 1600°, and then cooling rapidly in air; it cannot be formed
by heating the glass.

3. Of the four polymorphic forms of magnesium metasilicate, (I) is the stable form at all temperatures and the others are monotropic toward it, the order of stability being I, II, III, IV. This order is established by changing one form into another at various temperatures and by proving that (II) and (IV) change to (I) with evolution of heat. (III) has not been obtained in sufficient quantity for this test. Though enstatite and the amphiboles are not stable, any more than glasses are, on account of the great internal friction of the molecules, they have less tendency to change, when once formed, than many glasses. We cannot state definite limits of stability for the various minerals, as it is possible to do where the relation is enantiotropic; it is possible, however, to fix certain temperature limits below which one of these forms may crystallize from a melt of pure magnesium silicate. Thus enstatite could only form below about 1250°, since above that temperature it passes into the monoclinic form; but it must be remembered that in the silicate solutions of nature this limit would probably always be lower on account of the general occurrence in them of such compounds as ferrous silicate.

4. The specific gravities of the four forms, in the order of their stability, are : (I) monoclinic pyroxene, 3·192; (II) orthorhombic pyroxene (enstatite), 3·175; (III) monoclinic amphibole, not determined directly, but its relation to (II and (IV) is fixed by its index of refraction; (IV) orthorhombic amphibole, 2·857.

5. While our experiments do not settle completely the mysteries of the formation of unstable bodies, they do show that temperature and viscosity are two factors of prime importance. Thus, from melts or from silicate solutions, the stable monoclinic form of magnesium metasilicate crystallizes at the highest temperature, enstatite next, and the amphiboles probably lowest of all. From *thin solutions* the stable form is obtained at still lower temperatures, 800°–1000°, while from *aqueous solutions* at 375°–475° an amphibole results.

6. Our study of the Bishopville meteorite indicates that it must have been cooled very rapidly from a high initial temperature, and there is evidence that the same is true of other meteorites.

7. The intergrowths of enstatite with the monoclinic pyroxene, and of the two amphiboles, which we obtained in close resemblance to those of nature, are cases of falsee quilibrium, and their occurrence establishes the fact that it cannot be assumed that all rocks or mineral aggregates are systems in true equilibrium.

8. In the course of the investigation a useful method has been developed for detecting sluggish heat changes.

Geophysical Laboratory,
  Carnegie Institution of Washington, July, 1906.